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Kinetics of the reaction between thorium and water vapor

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Kinetics of the reaction between thorium and water vapor

Abstract

An examination of the reaction between thorium metal and water vapor has been made between the temperatures of 2000 to 600° C. and at water vapor pressures of 40, 70 and 100 mm. Hg. Analyses of the products have indicated that ThO₂ and H₂ are the main species formed during the reaction with thorium hydride as a possible side-reaction product. Two methods, gravimetric and manometric, were used successfully to determine the rates of reaction. During these rate studies three variables were examined: time, temperature and pressure. The reaction data were found to obey the logarithmic rate law $w = k \log(1 + 0.45t)$, where w = weight of water reacted per unit area of thorium surface, t = time and k is the rate constant.

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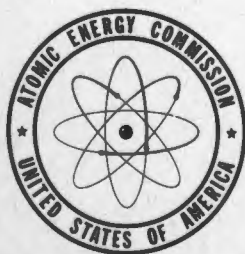
UNITED STATES ATOMIC ENERGY COMMISSION

**KINETICS OF THE REACTION BETWEEN
THORIUM AND WATER VAPOR**

By
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June 1955

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Ames, Iowa



Technical Information Extension, Oak Ridge, Tennessee

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F. S. Spedding, Director, Ames Laboratory

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BETWEEN THORIUM AND WATER VAPOR*

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Bruce E. Deal and Harry Svec

ABSTRACT

An examination of the reaction between thorium metal and water vapor has been made between the temperatures of 200° to 600° C. and at water vapor pressures of 40, 70 and 100 mm. Hg. Analyses of the products have indicated that ThO_2 and H_2 are the main species formed during the reaction with thorium hydride as a possible side-reaction product. Two methods, gravimetric and manometric, were used successfully to determine the rates of reaction. During these rate studies three variables were examined: time, temperature and pressure. The reaction data were found to obey the logarithmic rate law $w = k \log(1 + 0.45t)$, where w = weight of water reacted per unit area of thorium surface, t = time and k is the rate constant.

Three temperature regions have been examined in which different-appearing oxides were observed: 200° to 275°, black; 300° to 450°, gray or white; and 450° to 550°, metallic. The rate constants were found to be first order in dependence on water vapor pressure. The Arrhenius equation $\ln k = -E/RT + C$, where k = rate constant, E = activation energy, T = absolute temperature and R and C are constants, has been used to determine the activation energy. An average value of 6.44 ± 0.75 kcal./mole was calculated for the activation energy of the thorium-water vapor reactions. Several experiments were carried out in order to determine the reaction mechanism, and it has been postulated that inward diffusion of water molecules or a species thereof is the rate-determining step of the reaction. A value for the diffusion coefficient of water in ThO_2 was estimated to be approximately 10^{-7} cm.²/sec. Other experiments have shown hydrogen, produced by the reaction, to have diffused into the metal at the higher temperatures and lower pressures, thus causing erroneous results for rate constant values at those temperatures.

*This report is based on a Ph.D. thesis by Bruce E. Deal submitted June, 1955 to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

INTRODUCTION

Thorium was discovered by Berzelius in 1828, in the mineral thorite, the name of which was derived from Thor, a god of Scandinavian mythology. Little use was found for the element until 1880, when its demand by the incandescent gas mantle industry prompted a search for mineral sources of thorium and led to extensive research of its chemistry. However, the mantle industry has since declined to practically nothing, and it was not until the nuclear energy possibilities arose in 1940 that thorium has again emerged as an important element.

Fresh massive thorium is silvery white in color, but it quickly tarnishes in an atmosphere of water vapor above 150° C. with the formation of a black, white or gray film, depending on the temperature range. This film adheres to the metal surface during the first part of its formation acting as a protective layer. The process of film formation is similar to that which occurs when many metals react with oxygen gas or corrode in various liquid media. Considerable interest is attached to a better understanding of these processes, since they have such vast economic influences on our lives. For this reason a program was initiated to study the kinetics of the reaction of thorium with water vapor. This program included an examination of the rate at which the reaction occurs, the factors influencing the rate, the observation and identification of reaction products and an attempt to correlate the results of the study with those found for other gas-metal reactions.

REVIEW OF THE LITERATURE

Basic Information Concerning the Oxidation of Metals

General nature of oxidation reactions

In studying the nature and properties of metals, no pure metal has been found to be stable in air even at room temperature with the exception of gold. All metals tend to form oxides and many form nitrides and hydroxides. The kinetics of the reactions observed during these oxidation processes has been the object of extensive study. Correlation of many variables is necessary to explain observed reaction rates. These involve the characteristics of the metal and particularly the nature of the reaction-product film which is deposited on the metal surfaces.

Studies of many reactions between metals and gaseous oxygen and nitrogen have been reported in the literature. As a result of these studies, an extensive theory has developed to explain the observations.

The reaction between thorium metal and water vapor takes place with the formation of a reaction-product film on the metal surface, and thus rate observations should be explainable by the same laws governing reactions involving diatomic gases and metals.

In most complex chemical reactions which proceed by several simple successive steps the over-all rate is determined by the rate of the slowest step. Following Kubaschewski and Hopkins (1) a number of single steps may occur in a reaction between, for example, a metal Me and a gas A_2B to give the product MeB_4 as a growing layer.

1. Diffusion of A_2B to metal surface
2. Adsorption of A_2B on metal surface
3. Breaking of AB bond to form AB^- and A^+
4. Ionization of Me to Me^{+4} and electrons
5. Formation of species Me $[AB]_4$ from ions
6. Splitting out of A_2B to form MeB_4
7. Diffusion of A_2B inwards through growing coat
8. Diffusion of AB^- inwards through growing coat
9. Diffusion of Me^{+4} outwards through growing coat

It is clear from the above possibilities, that diffusion of some species through the product coating may play an important part in reactions of solids with gases. It would be of great value if diffusion rates of all systems involved in a particular gas-metal reaction were known, but unfortunately this is not the case. As a result much more experimental work remains to be done. Two basic diffusion laws are noteworthy. The first is Fick's law of diffusion which states that the amount of solute "w" diffusing through a certain cross-section "A" per second is proportional to the concentration gradient dc/dx at this plane:

$$\frac{dw}{dt} = D \frac{dc}{dx} \quad (1)$$

In this equation, "D" is the diffusion coefficient which is usually determined empirically. An expression more suited for measurements in solids is derived from the Boltzmann equation. It is

$$D = D_0 e^{-Q/RT} \quad (2)$$

D_0 and Q are constants, but their physical meaning is not fully understood.

If diffusion of some species in a surface oxidation is believed to be the rate-determining step, then a method of experimentally determining which species is diffusing would be of great value. It is generally assumed that the ion or molecule with the smaller diameter is best able to diffuse through a growing reaction coat. Since the radii of the common anions are relatively large, the metal ions are as a rule expected to diffuse outward and thus determine the rate of the reaction. However there have also been exceptions wherein the negative ion has definitely been the diffusion species. Such is the case with Fe_2O_3 , in which case the oxide grows entirely by diffusion of O^{2-} inward.

One of the primary aims, therefore, of studying gas-metal reactions is to attempt to determine the rate-determining step. To accomplish this the factors which influence the rate of this slow step and thus the over-all reaction must be known. Gulbransen (2) listed the following variables as being important in any systematic study of the oxidation process for a particular metal or alloy: time, temperature, pressure, surface preparation including chemical treatments, composition of the oxidizing atmosphere, composition of the inert gas in the lattice of the metal, crystal orientation in the metal surface, surface area, cycling procedures in temperature, rate of gas flow and vacuum effect. However, the three most important variables from the point of view of reaction kinetics are time, temperature and pressure.

Dependence of oxidation rates on temperature

Several laws have been proposed to explain the time variation of the oxidation of metals. The most important of these are the linear law, the parabolic law and the logarithmic or exponential law. In 1922 Tammann and Koster (3) found that the interference color changes on the surface of zinc heated to 400°C . in air followed an exponential law. This was stated

$$t = Ae^{by} - A, \quad (3)$$

where y = film thickness as obtained from the interference color observations, t = time and A and b are constants. The following year Pilling and Bedworth in a now classic work (4) proposed the linear and parabolic rate laws to explain the rate of oxidation of copper, cadmium, zinc and other metals at high temperatures. Which of these laws were applicable to a particular reaction depended upon the ratio of the molecular volume of the metallic oxide to that of the metal. Thus, for values of M_d/mD (where M is the molecular weight of the oxide; D , its density; m , the molecular weight of the metal; and d , its density) less than one,

the oxide coat is porous or may not adhere to the metal; and a linear law,

$$y = kt + A, \quad (4)$$

is followed. When this ratio is equal or slightly greater than one, an adherent oxide film is formed, and a parabolic rate law,

$$y^2 = kt + A, \quad (5)$$

is followed. In Equation 4 and 5 "k" is a constant and the other symbols are the same as those in Equation 1. Pilling and Bedworth were able to explain these laws on the basis of the fact that the rate-limiting step during the reaction was diffusion of some species in the reaction coat. Recently Wagner and Grunewald (5), Mott (6) and Miley (7) have proposed similar explanations for these two laws.

Bangham and Stafford in 1925 (8) observed that an empirical rate law,

$$dy/dt = kt^{-(1-A)}, \quad (6)$$

fitted the data obtained when zinc reacted with oxygen at temperatures below 400° C. The extensive investigation of this reaction by Vernon, Akeroyd and Stroud (9) was reported in 1939 for the temperature range 25° to 400° C. These workers found that a logarithmic law,

$$w = k \ln(at + c), \quad (7)$$

best fitted their data, where w = weight gain due to the oxide film; t = time; and k , a and c are constants. For c equal to unit, $1/a$ equal to A , w equal to y , and $1/k$ equal to k , this law is the same as that of Tammann and Koster. Thus the logarithmic law was discovered independently by Tammann and Koster in 1922 and by Vernon, Akeroyd and Stroud in 1939. Because Tammann's pioneering work was based on measurements obtained by a simple color method, the results were not considered highly accurate. Consequently, the work of Vernon attains considerable importance.

Recently other oxidation reactions have been found to follow the logarithmic law. Alexander and Pidgeon (10) studied the oxidation of titanium by oxygen at low temperatures and at gas pressures of 2 to 20 cm. Hg. They were able to fit their data to a logarithmic equation similar to that of Vernon. Brodsky and Cubicciotti (11) have found the the oxidation of silicon at high temperatures follows the logarithmic law. These workers, following the method of Tammann and Koster, derived the logarithmic law from Fick's law of diffusion. As stated above

$$\frac{dw}{dt} = D \frac{dc}{dx}, \quad (1)$$

where w = amount of diffused substance, c = concentration of the diffused species at a distance x from the starting point, t = time and D = the diffusion coefficient. If the diffusion of some species through the growing oxide layer is the rate-determining step for the reaction and if the diffusion paths through the oxide are blocked in some statistical manner, the concentration of the diffusing species in the coat will decrease exponentially. Stated mathematically,

$$c = c_0 e^{-bx}, \quad (8a)$$

where c_0 and b are constants. Therefore, the concentration gradient will be

$$\frac{dc}{dx} = -c_0 b e^{-bx}. \quad (8b)$$

Since the total thickness of the oxide, x , is related to w by a gravimetric factor ($w = gx$),

$$\frac{dw}{dt} = D \frac{dc}{dx} = -Dc_0 b e^{-wb/g}. \quad (8c)$$

Integrating,

$$w = g/b \ln [-Dc_0 b^2 t/g + c'] \quad (8d)$$

or

$$w = k \ln [at + c']. \quad (7)$$

The condition that when $w = 0$, $t = 0$, requires that $c' = 1$. Hence,

$$w = k \ln [1 + at], \quad (8e)$$

which is the logarithmic rate law.

At present, the exact mechanisms of the three oxidation laws are still not well established. However, Evans (12) summarized the various theories of these rate laws in 1943, and no major changes have as yet been proposed.

1. The Linear Law, $y = kt + A$, occurs when the films formed on metals are porous or non-continuous or in those cases where the film falls completely away from the metal as it is formed. Thus, a continually renewed metallic surface is available for reaction.

2. The Parabolic Law, $y^2 = kt + A$, is followed when non-porous films possessing ionic and electronic conductivity are formed and is governed by ionic migration under a potential gradient.

3. The Logarithmic Law, $y = k \log [at + c]$, is followed when the above conditions for the parabolic law are absent, and is believed to be due to the migration of interstitial matter through flaw-paths or zones of loose structure in the outer part of the oxide film. Thus, the actual rate of passage along a given path depends upon the rate of crossing a less pervious inner film of constant thickness and is independent of the thickness of the outer film, provided that no obstruction occurs in the path through the outer film. If such an obstruction occurs, however, passage along the path in question becomes impossible, and the change of obstruction of a given path will increase with the film thickness. It can be shown that the growth rate will fall off with film thickness in accordance with the logarithmic law.

Dependence of oxidation rates on temperature

Pilling and Bedworth (4) first formulated an empirical expression relating temperature and oxidation rate, but it was soon discarded since no physical significance could be attached to it. Later Dunn (13) applied the Arrhenius equation to the oxidation of metals as a function of temperature. The use of this equation,

$$\frac{d \ln k}{dT} = \frac{-Q}{RT^2} \quad \text{or } k = Ae^{-Q/RT}, \quad (9a)$$

where k = oxidation rate, T = absolute temperature and A and Q are constants, was justified by Dunn's work with several metals. Arrhenius (14) originally derived this equation starting with the van't Hoff equation. By taking the logarithm of each side of Equation 9a and setting Q equal to E , the relationship,

$$\ln k = -E/RT + \text{constant}, \quad (9b)$$

is observed where E is the energy of activation. E may be determined by plotting $\ln k$ against $1/T$ and solving for E from the slope, which is equal to $-E/R$. It is possible, therefore, to calculate a value for the energy of activation of a gas metal reaction, provided the Arrhenius equation is valid for the data.

Attempts have been made to attach some theoretical significance to the constant in the Arrhenius equation. Gulbransen (15) combined theories of Mott (16) and Eyring (17) which theory, when applied to diffusion processes, assumes the presence of a transition state at the top of an energy barrier between the initial and final states of diffusion, the transition states being in equilibrium with the initial state. He assumed the energy of activation E to be ΔF which is equal to $\Delta H - TAS$. The final equation, using an introduced term, kT/h , for the parabolic

rate law constant k_p is,

$$k_p = 2k'T/h d^2 e^{AS/R} e^{-\Delta H/RT}, \quad (10)$$

where k' = Boltzmann's constant, h = Plank's constant and d = the closest cation distance in cm. The significance of the various terms is reviewed by Gulbransen. Although it is tempting to derive an entropy as well as a heat term, the validity of Equation 10 has not been confirmed and much work must be done, both experimentally and theoretically, to prove its worth.

Dependence of oxidation rate on pressure

The dependence on gas pressure has been investigated for the oxidation of only a few metals. Depending on the mechanism and rate-determining step of the reaction, the gas pressure may or may not influence the reaction. Wilkins (18) suggested the idea of limiting pressures, both maximum and minimum, outside of which no definite rate law is followed. This type of range was observed to be true in the case of lithium-water vapor reactions (19). Barrer (20) has proposed two possible rate-pressure relationships for the diffusion of gases into metals or solids. For activated diffusion without dissociation the equation is

$$k = Cpe^{-b/T} + D \quad (11a)$$

and for diffusion with dissociation,

$$k = -Cp^{1/2}e^{-b/T} + D, \quad (11b)$$

where k = rate constant; p = pressure; T = temperature; and C , b and D are constants. Equation 11b would be expected for a diatomic gas, while 11a would be true for any gas not dissociating before diffusing. It may be noted that the above equations are very similar to the Arrhenius relationship (Equation 9a).

Experimental Methods

Methods of measurement

The gravimetric method is the most common method for the determination of oxidation rates because of its directness and general convenience. In its simplest form it consists of a furnace and an accurate balance. However, the best results have been obtained by using some form of the quartz-fiber microbalance or a quartz-spring balance. In these types of systems successive readings may be made, and a much more complete set of data can be collected.

A second method of studying metal oxidations is the manometric method. The apparatus consists essentially of a heated reaction tube, a gas supply and a manometer. The reaction may be followed either by the disappearance of the reacting gas or the evolution of a reaction-product gas. Naturally, in the former the reaction products must not include a gas, and in the latter the reacting gas must be maintained at a constant pressure. When using the manometric method, one must be certain that any evolved gas being measured does not react with the metal sample. If proper techniques are carried out, this method is as good or better than the gravimetric method when studying certain gas-metal reactions.

Other techniques used in the past might be mentioned. One is the electrometric method, which consists of determining the quantity of electricity needed to reduce the oxidation product to the metallic state. There are several optical methods as, the interference measurement of light on very thin films, polarized light measurements and transparency measurements. Also electrical resistance, stripped film and vacuum fusion measurements have been used.

Methods for examination of reaction products

Since a great deal of information about the nature and mechanism of a gas-metal reaction can be obtained by examining the reaction products, the various methods of examining metallic surfaces are important in the field of surface reactions.

The X-ray method can be used in studying oxidation products on metals to give information relating to identification, crystal size and orientation and the measurement of lattice parameters. The method is especially suitable for examining thicker reaction-product coatings. If these are removed from the metal, the ground powder can be used as the specimen. Glancing angle and back reflection techniques can be used while the oxide is still attached to the metal.

The electron diffraction method has been used to a considerable extent for the examination of oxide films on metals and is a well-recognized tool for the identification of such films. It is particularly suitable for the examination of the thinner oxide layers because the depth of penetration of the electrons is small.

Microscopic examination of oxide scale on metals is a useful method of providing information on the characteristics of the oxide and the mechanism of growth. Pfeil's work (21) on the mechanism of oxidation of ferritic materials was done largely by microscopic examination. In particular, he showed the importance of outward diffusion of metal in a growing oxide layer by examining an inert chromic oxide marker on the

original surface. Similarly, Davies, Simnad and Birchenall (22) have observed inward diffusion of anions in the oxidation of iron using platinum markers. The detection of layer formation in oxides is an obvious example of the use of the microscopic technique. Location, distribution, grain size, shape and other metallographic characteristics of oxides formed on metals are also features that are observed microscopically.

Other experimental techniques used in film observation are stripping of oxides, chemical analysis, emission spectrographic analysis and radioactive or isotopic tracer analysis.

Physical Properties of Thorium

The physical as well as chemical properties of thorium are described in detail by several authors (23, 24, 25, and 26). Table 1 lists the important physical properties of thorium metal along with X-ray data of compounds investigated in this research.

Table 1. Physical constants pertaining to the reaction between thorium and water vapor

<u>Compound</u>	<u>Symmetry system</u>	<u>X-ray Data</u>		
		<u>Lattice dimensions</u>	<u>Density, gm./cc.</u>	<u>No. stoichiometric molecules</u>
Th	Cubic	$a = 5.075$	11.71	4
ThH ₂	Tetragonal	$a_1 = 4.10$ $a_3 = 5.03$	9.20	2
ThH _{3.75}	Cubic	$a = 9.09$	8.25	16
ThO ₂	Cubic	$a = 5.5859$	10.00	4

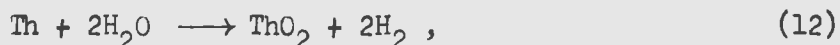
Physical Properties of Thorium

Atomic weight	232.12
Atomic number	90
Density (X-ray data)	11.7
Melting point	1450° - 1850° C.
Boiling point	greater than 3000° C.
Specific heat	26.8 joules/gm. atom ° C.
Coefficient of expansion	12.4×10^{-6} (25° - 1000° C.)
Thermal conductivity	0.33 watts/cm./° C. (100° - 300° C.)
Electrical resistivity	18.0×10^{-6} ohm-cm. (20° C.)

EXPERIMENTAL INVESTIGATION

Apparatus

It was found that the reaction between thorium metal and water vapor could be followed by measuring the pressure increase due to evolved hydrogen in a closed system. This fact follows from the reaction



which indicates that hydrogen is produced quantitatively. The rate of the above reaction was determined by introducing water into a suitable evacuated system containing thorium metal and measuring the pressure change. A similar technique was used for lithium-water vapor reaction studies (19). The thorium apparatus is shown in Figure 1. The reaction tube A was constructed of 25-mm.-diameter vycor and 30 cm. in length. The thorium sample B was suspended in the reaction tube by means of a stainless steel support. Around the reaction tube was a furnace C. A block diagram of the furnace-temperature control is shown in Figure 2. The furnace had a Chromel-A heating winding and a platinum temperature-sensing winding. At E was a water inlet tube. A serum bottle rubber stopper was at the top of the inlet tube, covered with a pool of mercury through which water could be injected into the system by means of a hypodermic syringe. Stopcock H led to an 18-mm.-bore calibrating manometer F and through stopcock K to a two-stage Hg diffusion pumping system.

A recording mercurial manometer D, following the design of Svec and Gibbs (27), was used to continuously measure the total gas pressure in the system. It consisted of a large bulb mercury manometer with a length of resistance wire (No. 30 Chromel-A) placed concentrically in the mercury column. The resistance wire was included in a direct current bridge circuit shown in Figure 3. The degree of unbalance of the bridge was followed with a recording potentiometer. Operation of the device required that the bridge first be balanced when the pressure in the apparatus was zero. Then, as the mercury column rose due to increasing pressure, the resistance of the concentric wire decreased, causing the potentiometer pen to drive up scale. From a suitable calibration curve, chart readings were converted to pressure. A slowly increasing gas pressure could thus be followed over a period of several hours.

With the exception of the reaction tube, the entire system was wrapped with electrical-resistance heating tapes. The water vapor pressure could, therefore, be controlled by the degree of current in the tapes, with the coldest spot determining the exact value. A calibration

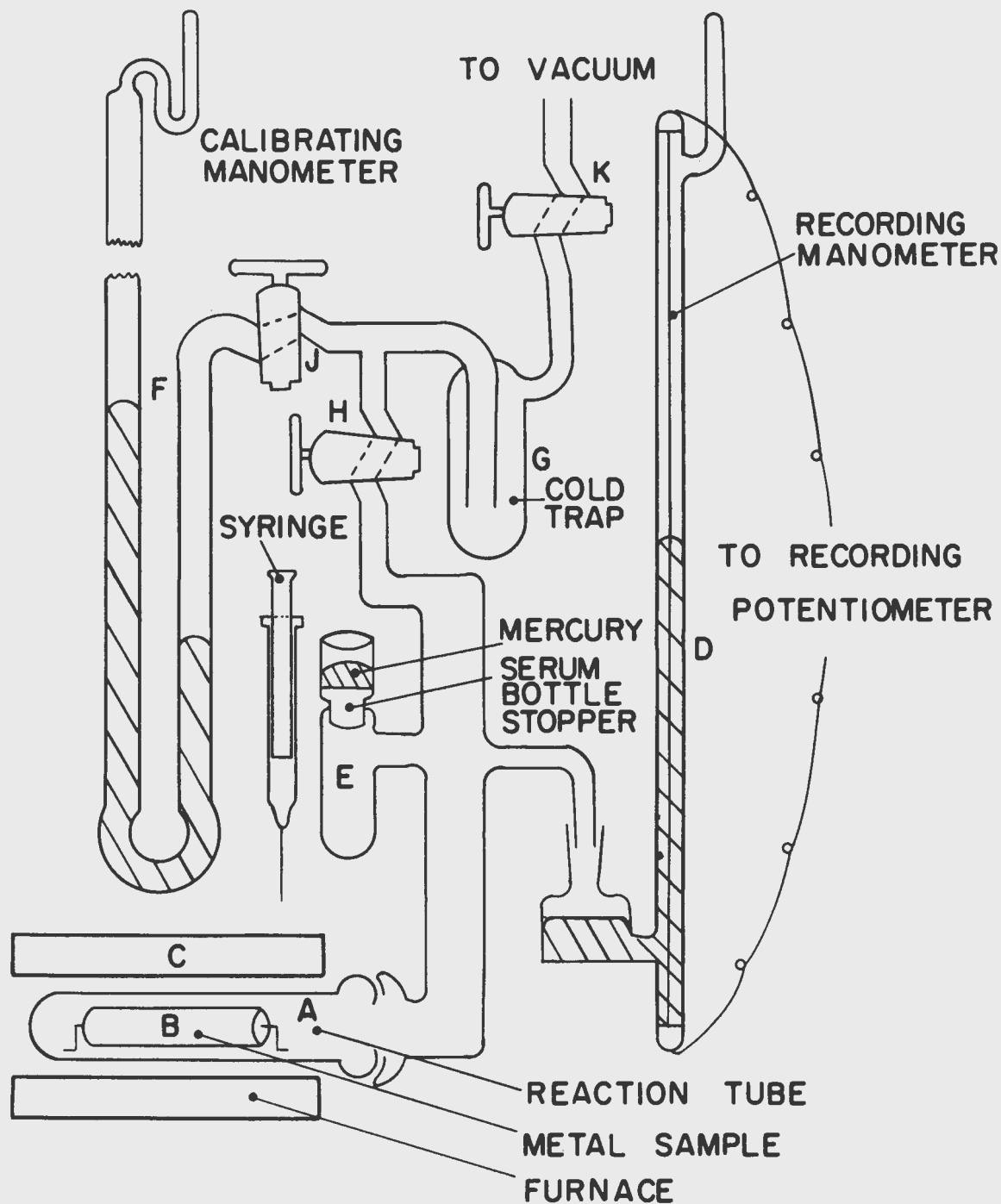


Figure 1. Manometric apparatus for studying the kinetics of the reaction between thorium and water vapor

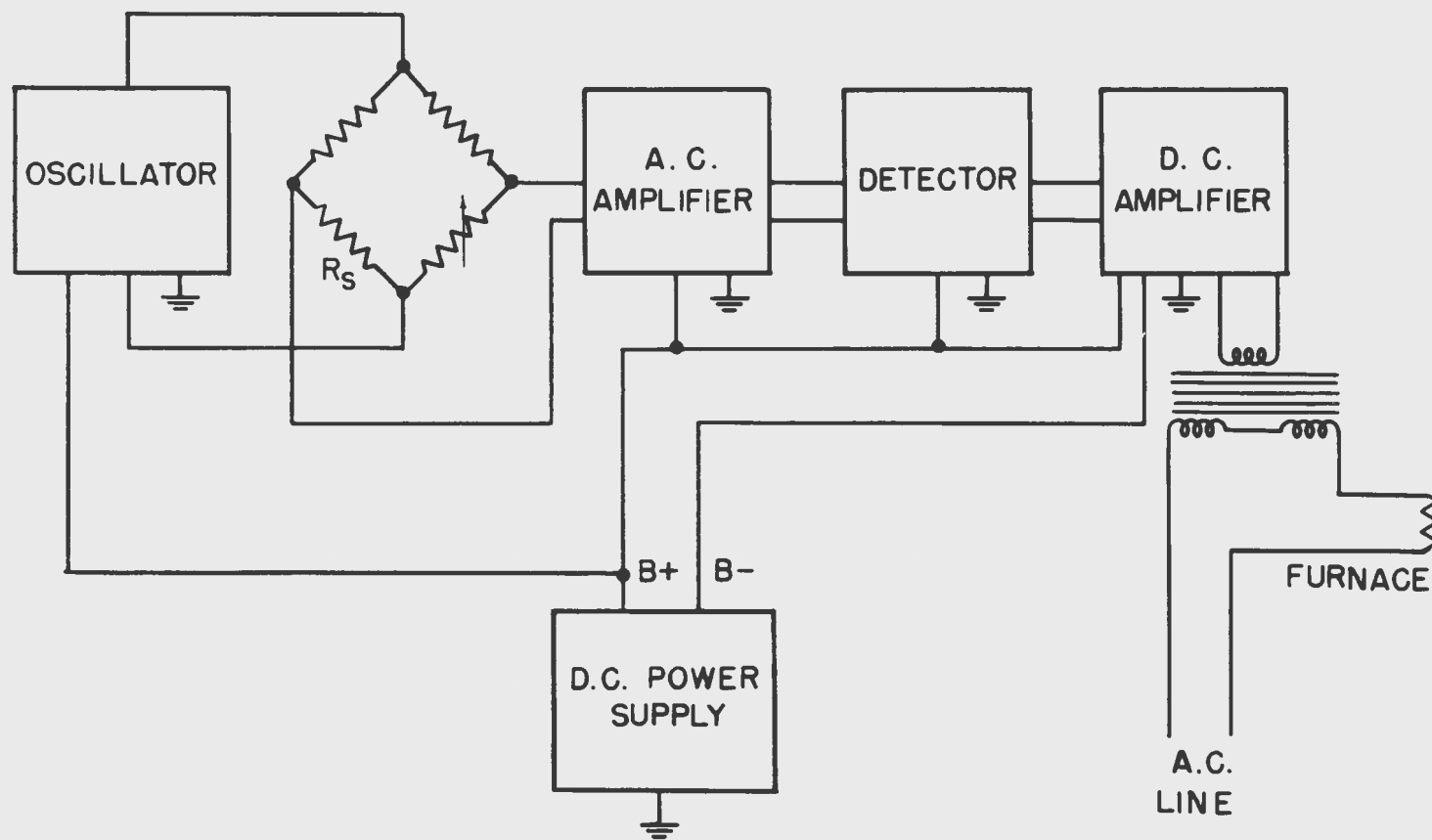


Figure 2. Block diagram of furnace-temperature controller
 (R_s = Pt temperature-sensing furnace winding)

was made whereby different vapor pressures of water could be reproduced. The furnace was also calibrated and the reaction temperature was measured by means of a calibrated thermocouple and a recording potentiometer.

In order to test the validity of the manometric apparatus results, a second apparatus was constructed by which the reaction rates could be studied by direct weight-gain measurements. It consisted essentially of a quartz microbalance enclosed in a glass vacuum system as shown in Figure 4. The quartz fiber microbalance C was similar in principle to that of Edwards and Baldwin (28) with the main difference being the heavier capacity with a consequent lower sensitivity. The balance load in these experiments was approximately 5 gm. on each side of the beam and weighings were made to 1/100 mg. The balance beam consisted of a 4-mm. quartz tube 16 cm. in length. A Cunife magnet approximately 3 mm. in diameter and 2 cm. in length was placed inside the beam equidistant from both ends. Quartz fibers were pulled from each side of the beam at its center and fastened to a supporting quartz frame. Hooks were placed on each end of the beam from which weights could be suspended.

The position of the balance beam could be electromagnetically controlled by current flowing through two coils of No. 26 heavy Formvar magnet wire, placed above and below the balance as shown in the figure at D. The coils, mounted on two clear plastic spools (Lucite), were approximately 4 1/2 inches in diameter and consisted of 1500 turns each. The resistance of each coil was 58 ohms. They were connected in series with a 100,000 ohm variable decade resistance box, a 22 1/2-volt battery and a 4.56-ohm constantan wire resistor. Accurate measurement of current was made by measuring the IR drop across this resistor by means of a potentiometer. The balance was calibrated by measuring the amount of current required to raise each of a set of precision weights back to a selected null point, and all subsequent measurements employed the null method. A plot of millivolts (potentiometer readings) versus milligrams was made and a straight line was obtained for weights of 0 to 50 mg. As was reported by Edwards, an approximate relationship of 1 ma. to 1 mg. was observed.

The balance was enclosed in a water-jacketed glass tube approximately 25 mm. in diameter and 35 cm. in length. The water was ~~as~~ circulated through the jacket from a constant temperature bath. It was allowed to enter the jacket by gravity flow and then to empty into a Dewar flask. A circulating pump pumped the water back into the bath. No pump vibration was transmitted to the balance. A total temperature drop of only three degrees was observed in the returning water.

An arm extended from each end of the balance container, in which the weights could be supported at A and B. At A thorium cylinders were

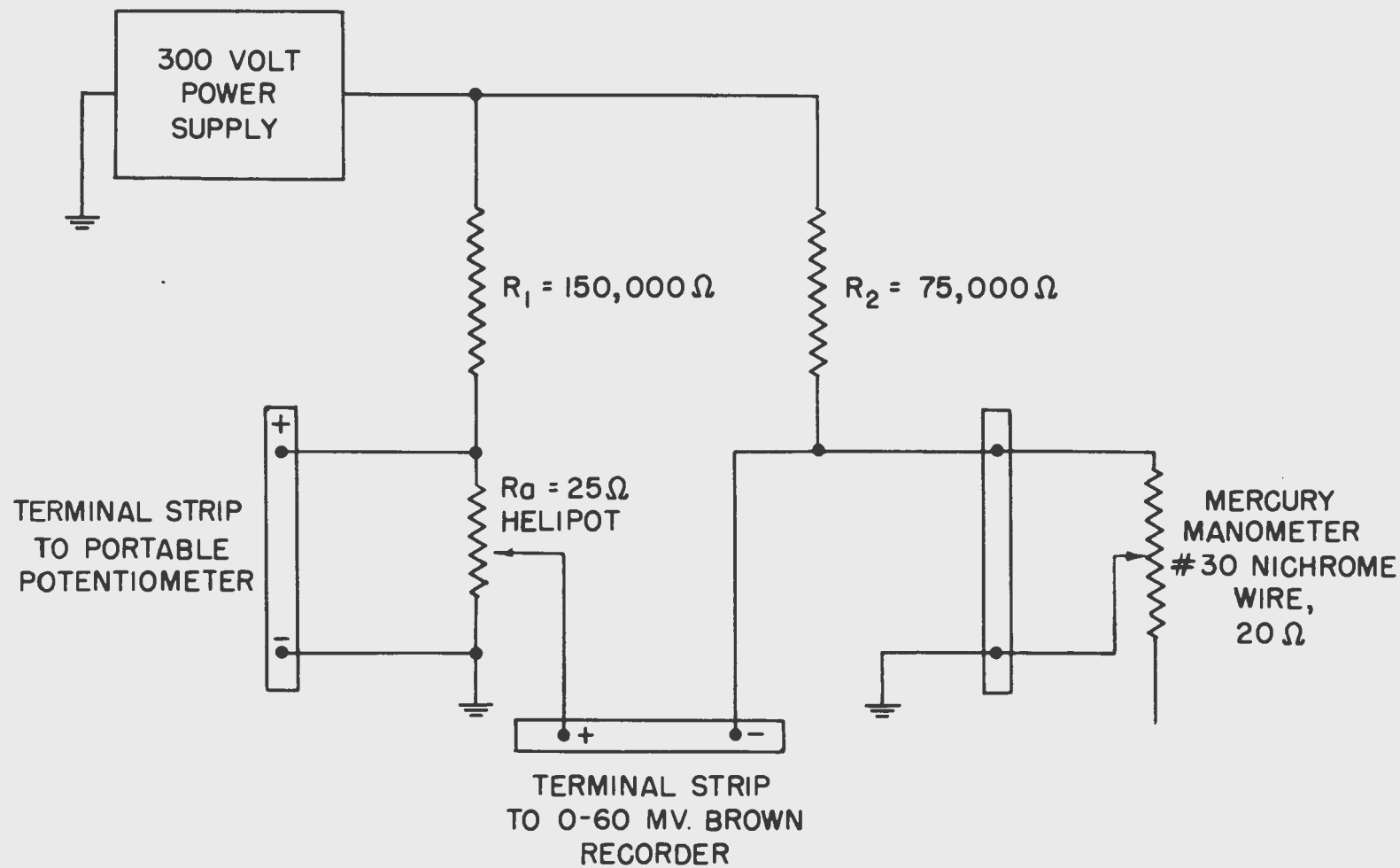


Figure 3. Schematic diagram of recording mercurial manometer

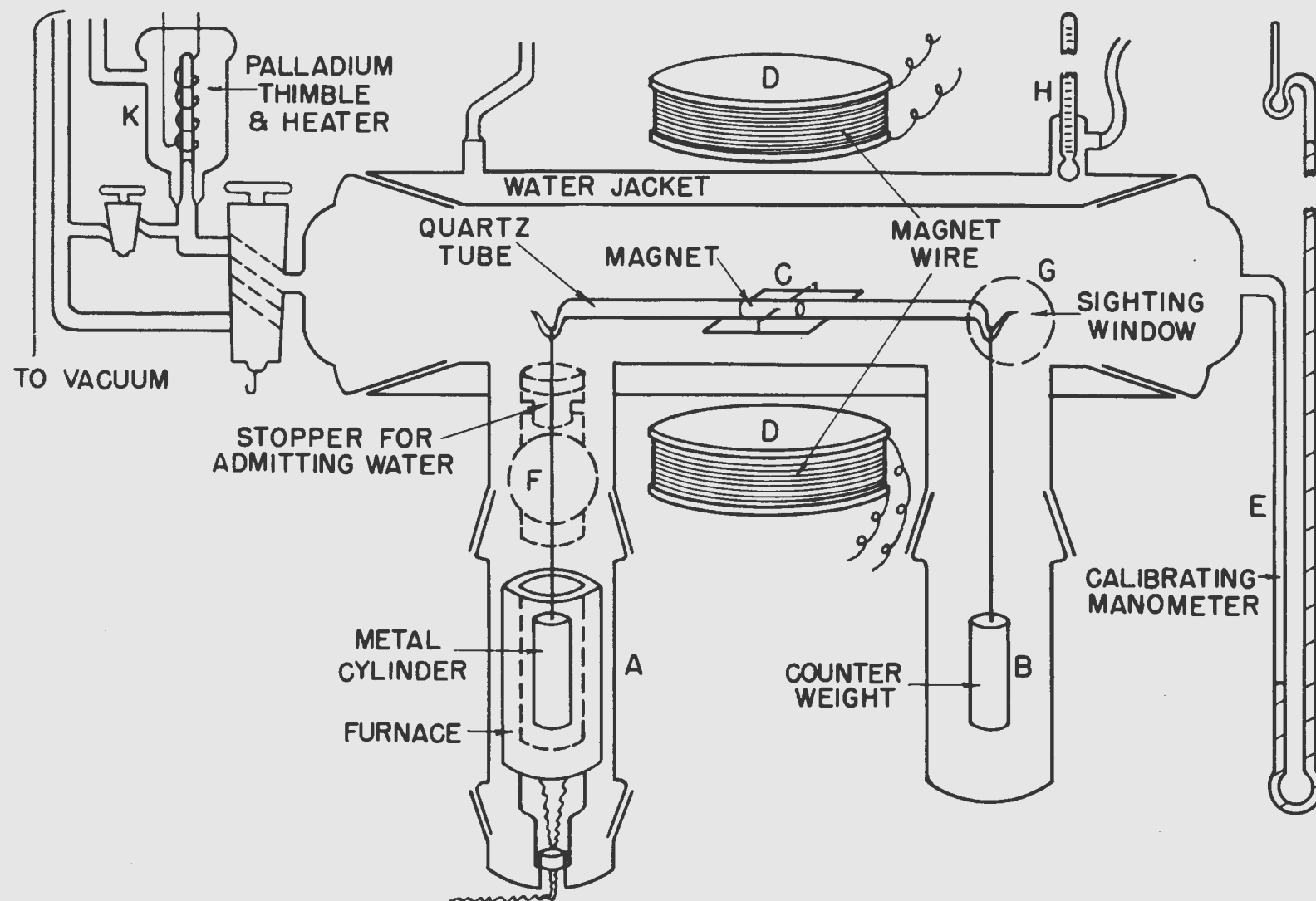


Figure 4. Gravimetric apparatus for studying the kinetics of the reaction between thorium and water vapor

suspended and situated inside a small furnace. This furnace, shown in Figure 5, consisted of a special core, 17 mm. in diameter and 7 cm. in length, fabricated from lava and fired at 1000°C . The temperature control circuit, the diagram of which is shown in Figure 3, was the same as that used for the manometric-apparatus furnace. Windings of No. 30 Nichrome and 0.005-inch-diameter platinum were wound on the lava core in a double set of 1/16-inch threads, with 1/32-inch spacings between the platinum and Nichrome wires. A Nichrome shield was placed around the windings, and the furnace was supported from a standard taper as shown in Figure 5. A calibration was made for the furnace from 100° to 600°C .

The rest of the system consisted of a water inlet tube F with a serum bottle stopper and pool of mercury for admitting water into the system; a double sighting window G, through which the balance could be zeroed by the crosshairs of a measuring microscope; a thermometer H for measuring the temperature of the water circulating through the jacket; and a pressure-calibrating manometer E. All parts of the system not heated by the circulating water were wrapped with heating tapes. As was the case in the manometric system, the vapor pressure was controlled by the amount of current flowing through the tapes, with the coldest spot determining the vapor pressure value. Two photographs of the system are shown in Figure 6.

As indicated in Equation 12, the reaction between thorium and water vapor produces hydrogen. Since it was not known whether the evolved hydrogen entered into the reaction, the evolved hydrogen was removed in some of the runs to determine any effect the absence of hydrogen might have. It has been reported (29) that at temperatures of 250° or above, palladium will permit hydrogen from a higher pressure to diffuse through it to a lower pressure. This principle was utilized at K in the figure. A palladium thimble, .001 inches thick, about 6 cm. in length and 6 mm. in outside diameter, was placed between the reaction system and the vacuum system. It was mounted in a converted Type 507 ion vacuum gauge making use of the spiral grid as a heater which was connected to a variac. The filament of the gauge was removed and a Chromel-Alumel thermocouple was attached to the filament leads. Thus the temperature of the heating coil could be measured at any time. By heating the thimble to 300° and closing the system to the direct vacuum lead, any hydrogen evolved in the reaction could readily be removed through the palladium without affecting the water vapor.

Procedure

Thorium metal was obtained from the Ames Laboratory of the Atomic Energy Commission in the form of a large billet. Spectrographic analysis previously made by the analytical section of the Ames

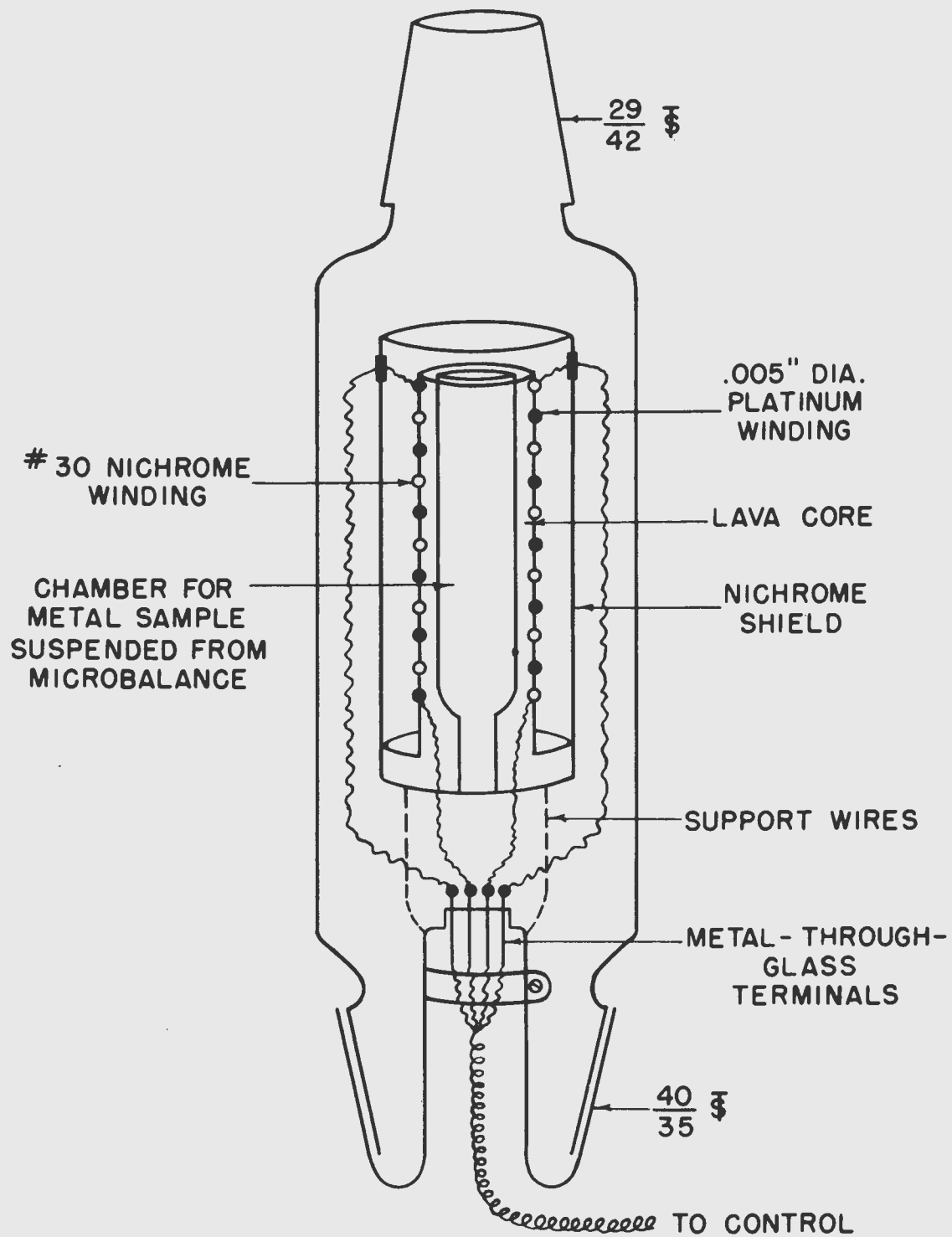


Figure 5. Furnace contained in gravimetric apparatus

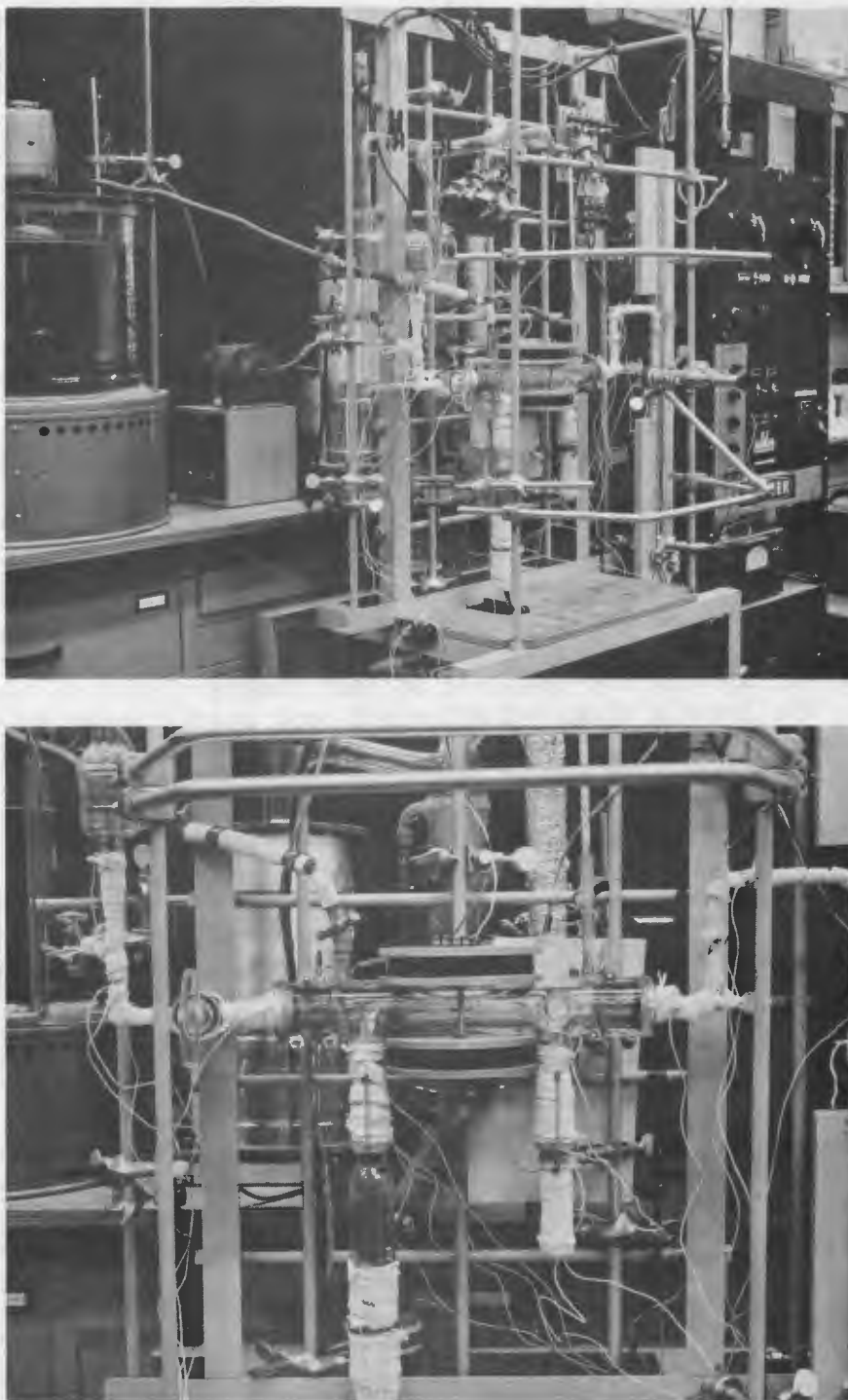


Figure 6. Gravimetric apparatus. Top photo shows entire apparatus while lower photo is of microbalance and reaction system

laboratory indicated that the total impurities were as follows:

C	410.0 - 420.0 ppm	Be	60.0 ppm
N	158.0 - 155.0	Ca	< 50.0
B	< 0.5	Mg	< 20.0
Cd	< 0.2	Si	< 50.0
Zn	< 20.0	Fe	105.0
Al	< 25.0	Mn	< 20.0

Cylinders approximately 2 inches in length and 1/2 inch in diameter were prepared for the manometric runs. For the gravimetric experiments the dimensions of the cylinders were 3/4 inch in length and 1/5 inch in diameter. They were prepared by machining under sodium-dried turbine oil. Machining conditions were carefully controlled and repeated for each cylinder to insure a uniform metal surface for the entire group of samples used in this study. As a result of these precautions, a smooth-appearing, shiny surface was obtained on the cylinders with no apparent tarnishing. The freshly machined cylinders were stored under sodium-dried turbine oil until used. All handling of the cylinders was by means of rubber-tipped forceps or surgical gloves which had been dipped in dry turbine oil. This precaution was necessary to obviate the formation of active centers on the metal surface.

Immediately preceding the experimental reactions, the dimensions of the cylinders were measured using machinists' calipers; and, in the case of the gravimetric runs, the cylinders were weighed after removing the oil from the thorium. The oil was removed using a rinse of sodium-dried S kelly B followed by one in sodium-dried diethyl ether. During this latter rinse operation, the cylinders were placed in the appropriate support, depending on the type of experiment. For the manometric experiments, the cylinder and support were placed in the reaction tube, the tube connected to the system and the system evacuated. For the gravimetric run, an appropriate stainless steel counter-weight was selected and the two objects were suspended from the balance beam. The side arms, one containing the microfurnace, were attached to the system, and the system was evacuated.

In both types of experiments the evacuation was continued for 1 hour, in which time the furnaces and heating tapes reached the desired temperatures. At this time each system was closed to the vacuum pumps and water introduced through the inlet tube. For the manometric run, the potentiometer pen had previously been zeroed at a chart reading

already selected when calibrating the manometer; and as the reaction between water vapor and thorium proceeded, the pressure of the hydrogen evolved was recorded. For the gravimetric system reaction, a zero weight reading (in millivolts) for the microbalance was obtained before adding the water. A stopwatch was started at the time of addition of the water and readings of the current required to null the microbalance were taken at 5-minute intervals. Reactions were followed for about 45 to 60 minutes for both of the systems.

Because two of the rate variables, vapor pressure and temperature, are not independent, it was necessary to be able to vary one and hold the other constant. This was accomplished by means of the variable furnace and the variable heating tapes. The vapor pressure, in both systems, could be held constant while the reaction temperature was varied from 100° to 600° C. Similarly, the temperature of the reacting thorium could be held constant while the vapor pressure was changed from 25 to 100 mm. Hg for a series of runs. In calculating the thorium oxide weight gain from the hydrogen gas pressures, a correction had to be applied for the differences of temperature in the two parts of the manometric system.

Several analyses of the reaction products were made using powder X-ray diffraction, surface X-ray diffraction and spectrographic analysis. A vacuum fusion technique was used to detect the presence of adsorbed or absorbed gases, followed by mass spectrometric analysis of the gases. A series of runs were carried out in the manometric system using D₂O rather than H₂O vapor. For mechanism studies, a 0.05-inch diameter platinum wire was securely placed vertically into the side of a thorium cylinder and the end of the wire machined even with the thorium surface. The relationship of the end of the wire to the thorium surface could be observed microscopically after a regular reaction with water vapor.

EXPERIMENTAL RESULTS AND DISCUSSION

Examination of Reaction Products

As the various manometric reactions between thorium and water vapor proceeded, the following observations were made. The pressure due to the liberated hydrogen increased slowly, and it appeared that a protective film was being formed. Over a temperature range from 200° to 600° C. different-appearing products were observed. From 200° to 275° a dull-black coat was formed on the thorium sample which did not change in color over a period of 2 or more hours. After an hour, however, the material started to powder and fall from the sample. Between 300° and 450° the color of the growing layer was either gray or white, with the whitest product being at 375°. At 500° the product appeared to be almost metallic in nature, while at 600° the gray material was observed

again. No differences in appearance were observed, however, at any one temperature when the reactions were carried out under different water vapor pressures.

In order to know the composition of these reaction products, samples of the coat were scraped off as powder and X-ray pictures were taken in a powder camera by the Ames Laboratory X-ray group. It was possible to secure powder samples only up to 450° , but the powder patterns of all samples taken were identical with that obtained employing an authentic ThO_2 sample. For information concerning the entire temperature range, rectangular specimens of thorium metal were prepared and water vapor reactions carried out at 250° , 350° and 500° . Each temperature corresponded to one of the color variations of reaction product. These samples were then analyzed by means of a recording X-ray diffractometer. Two sample regions of the results are shown in Figures 7 and 8. All peaks are attributed to either ThO_2 or thorium metal and show identical lattice constants for all three samples. However, there is a marked difference in the intensity and distinctness of the peaks. Going from a low to high temperature it is clearly observed that the 20 values vary from low, indistinct peaks to sharp, well-defined ones. As was the case with the LiOH coating (19), the low, broad peaks are believed to indicate extremely small crystals, while the sharp peaks in the higher temperature range show that a larger, more perfect crystal is present.

Another check made on the products of the thorium-water vapor reaction was an analysis of the gas produced. A sample of the gas was collected, the water vapor frozen out and the remaining gas analyzed in a mass spectrometer. Only hydrogen was found to be present in the mass spectra except for a trace of residual water vapor.

It was observed that at 500° or above, a silvery material was deposited just outside the furnace on the inside of the reaction tube. Samples of this material were collected and analyzed spectrographically. The analysis showed the following elements to be present: thorium, 50 per cent; cadmium, 30 per cent; and zinc, 20 per cent. It is surprising that thorium should distill off at as low a temperature as 500° , but evidently some intermetallic compound is formed. Samples of the thorium which had been reacted at 500° were machined and allowed to react at a lower temperature. No apparent difference in rate was observed when compared to other reactions of different cylinders at the same temperature and pressure.

Rate Law Determinations

Since the reaction of thorium with water vapor proceeds with the formation of a ThO_2 surface film, the reaction-rate data are expected to fit one of the three gas-solid rate laws stated in Equations 4, 5 or 6. A comparison of these three laws is presented in Figure 9 to

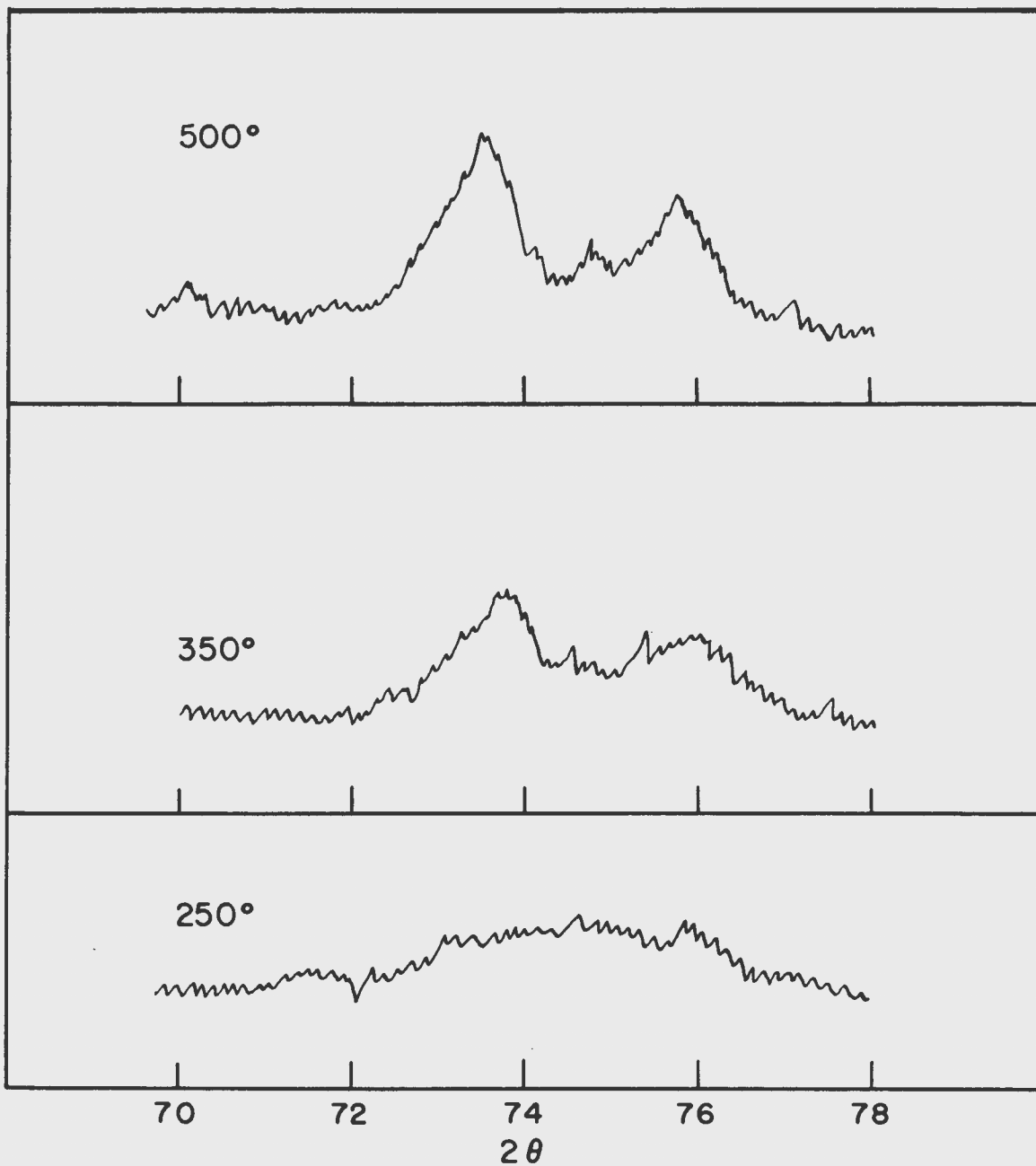


Figure 7. X-ray diffraction recordings of thorium-water vapor reaction products showing 2θ values between 70° and 80°

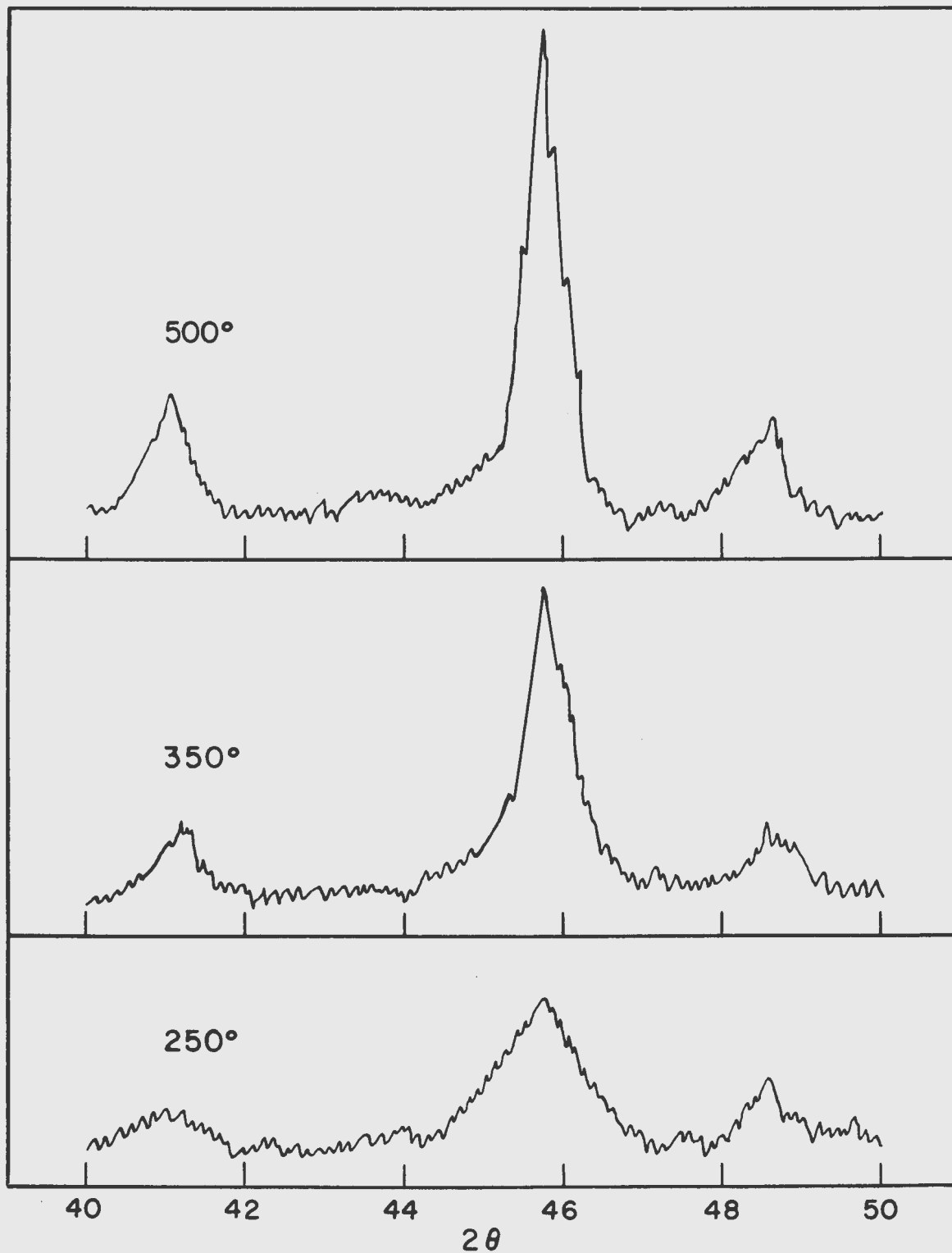


Figure 8. X-ray diffraction recordings of thorium-water vapor reaction products showing 2θ values between 40° and 50°

determine which law best describes the data obtained from a typical manometric experiment. The weight of water vapor in milligrams reacted per cm^2 of thorium surface is plotted against the appropriate function of time. The water vapor, weight values were obtained from hydrogen pressures by determining the total volume of the reaction system, the volume and surface area of the thorium cylinders and then utilizing the ratio of hydrogen produced to water vapor reacted as determined from the chemical equation involving the reaction of thorium with water vapor. The hydrogen pressures were obtained by subtracting the vapor pressures of water at the temperature being studied from the total pressure. In converting from hydrogen pressure to milligrams of water reacted, it was necessary to take into account the higher temperature of the reaction tube.

It was assumed that the surface areas used for these calculations were only minimum areas and thus the rate constants were maximum in value. The areas could well have had actual values equal to twice those which were calculated, due to surface unevenness formed in the machining process and to the nature of the metal. Additional work on the true surface area determination of machined metals is needed to obtain absolute rate constants. It was assumed, however, that the true surface areas were proportional to the calculated areas by a fairly constant factor. This was substantiated by the reproducibility of the data obtained from both the manometric and gravimetric experiments. From Figure 9 a straight line is observed for the logarithmic treatment of the data. The curves, concave upward for the parabolic plot and concave downward for the linear plot, emphasize the conclusion that a logarithmic rate law is followed. Similar plots of data from other experiments corroborate this conclusion.

The value of the constant "a" in the logarithmic equation was set equal to 0.40 by Brodsky and Cubicciotti (11) in silicon-oxygen reaction rate studies, but its magnitude under the conditions of this research was empirically determined by finding that value which best fitted the experimental data. Different values of "a," ranging from 0.20 to 0.80, were applied in a series of plots involving the weight of water reacted versus the logarithmic time function. As shown in Figure 10, a value of 0.45 provided the best of the straight lines obtained, although the function is relatively insensitive to the value of "a."

Temperature and Pressure Dependence

Graphs were prepared for each reaction which contained mg. H_2O reacted per cm^2 thorium plotted against $\log [1 + 0.45t]$, where "t" is the time in hours. Values of the logarithmic rate constants "k" were found as the slopes of the initial part of the curves, where definite straight lines were evident. Table 2 lists the slopes in $\text{mg./cm}^2\text{-log hours}$ for each manometric run and lists the average slopes at each

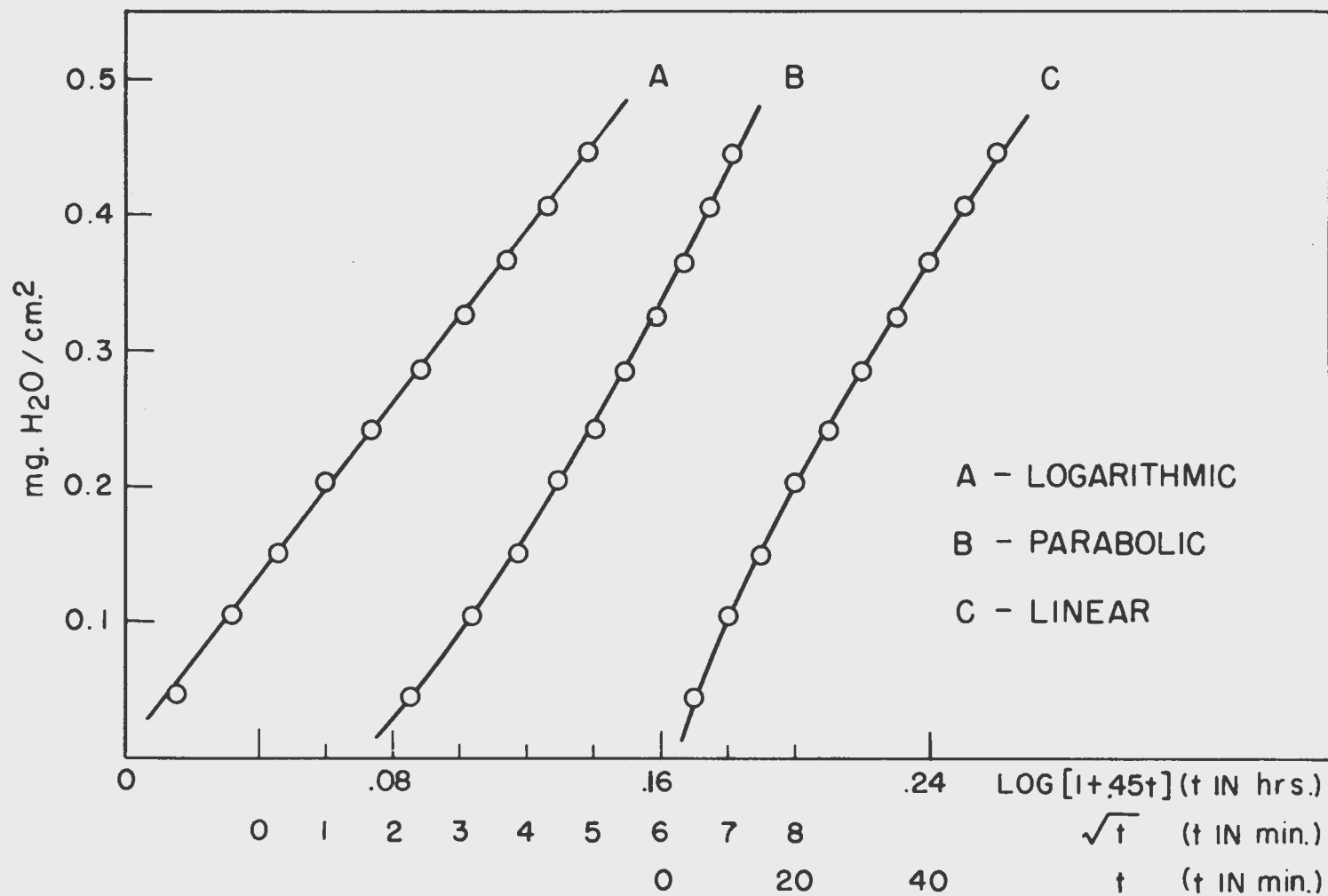


Figure 9. Comparison of three rate laws for gas-metal reactions using thorium-water vapor data

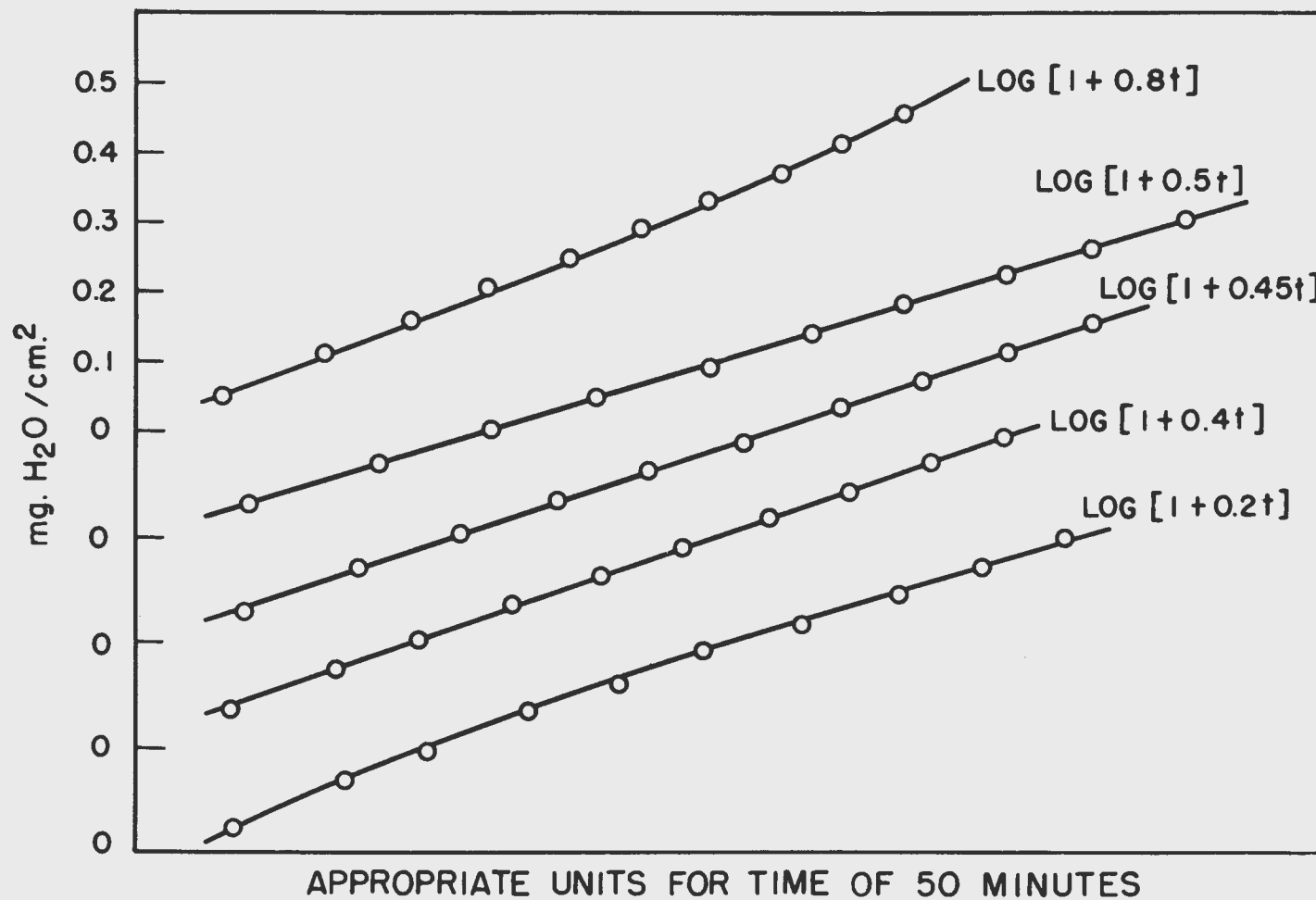


Figure 10. Comparison of values for the constant "a" in logarithmic rate law using thorium-water vapor data

temperature and water vapor pressure. Table 3 gives similar information for some thorium-heavy water vapor manometric runs, as does Table 4 for thorium-water vapor gravimetric reactions. The heavy water vapor pressures were corrected by adjusting current in the heating tapes, as required by the difference in H_2O and D_2O vapor pressure-temperature relationships (30).

Typical examples of the plots are shown in Figures 11 and 12. Figure 11 contains plots of the reaction data for a constant water vapor pressure of 70 mm. Hg and over a series of temperatures from 200° to 400° C. Two distinct regions are indicated by the use of two different symbols, corresponding to the black oxide formed from 200° to 275° and the white or gray oxide formed from 300° to 400° . Figure 12 indicates that the reactions are both pressure and temperature dependent in the range studied. The figure contains plots of the data at 300° and over a water vapor pressure range of 25 mm. to 100 mm. Hg. A more complete picture of the temperature and pressure dependence of the thorium-water reactions may be observed in Figures 13 and 14. In Figure 13 the three reaction-product regions are clearly indicated by the plots of rate constants versus temperature. At each of the three pressures the reaction rates uniformly increase from 200° to 275° , at which point they suddenly drop. After a slight minimum, the rates again increase with 40-mm. range reaching a maximum at 350° , followed by a minimum at 500° . The other two pressure ranges are similar, the 70-mm. range having a maximum rate constant at 400° and a minimum at 550° and the 100-mm. range having a maximum and minimum at 435° and 600° , respectively.

Rate constants are plotted against water vapor pressures in Figure 14, and a pressure dependence is observed over the entire temperature range studied. Plots were made involving various functions of pressure, such as P , P^2 and $P^{1/2}$. The best straight lines were obtained using the first power of pressure. Thus the pressure dependence is first order.

Activation Energy Determinations

It was stated that a form of the Arrhenius expression, Equation 9b, could be used to determine the activation energy for the thorium-water vapor reaction. This is accomplished by plotting $\log k$ against $1/T$ and determining the slope, where " k " is the rate constant and " T " the absolute temperature. " E ," the activation energy, is equal to $-2.303 \times R \times \text{slope}$. Three different water vapor pressures, 40, 70 and 100 mm. Hg, were utilized in the reactions. Plots of $\log k$ versus $1/T$ are shown for these three pressure ranges in Figures 15, 16 and 17. Figure 15 shows the plotted data for both manometric and gravimetric methods at 40 mm., with the straight lines being drawn to fit the manometric data only. The two differing reaction-product regions are

Table 2. Manometric thorium-water vapor reaction data

Run	Temp., ° C.	Vapor pressure, mm. Hg	Slope K, mm./cm. ² -log hr.	Average slope k, mg./cm. ² -log hr.
I-1	200.0	40	1.56	1.53
I-2			1.50	
II-1		70	2.25	2.12
II-2			2.00	
III-1		100	3.33	3.15
III-2			2.96	
IV-1	225.0	40	2.00	1.88
IV-2			1.76	
V-1		70	3.58	3.20
V-2			2.82	
VI-1		100	5.40	5.20
VI-2			5.00	
VII-1	250.0	40	2.60	2.55
VII-2			2.50	
VIII-1		70	5.00	5.00
VIII-2			5.00	
IX-1		100	6.70	6.42
IX-2			6.15	
X-1	275.0	40	3.25	2.82
X-2			2.40	
XI-1		70	6.15	5.71
XI-2			5.28	
XII-1		100	7.27	6.59
XII-2			5.50	
XII-3			7.00	
XIII-1	300.0	40	2.94	3.18
XIII-2			2.86	
XIII-3			3.75	
XIV-1		70	5.25	5.42
XIV-2			5.38	
XIV-3			5.62	
XV-1		100	8.33	7.91
XV-2			7.50	

Table 2 (Continued)

Run	Temp., ° C.	Vapor pressure, mm. Hg	Slope K, mm./cm. ² -log hr.	Average slope k, mg./cm. ² -log hr.
XVI-1	350.0	40	5.25	5.12
XVI-2			5.00	
XVII-1		70	9.52	9.76
XVII-2			10.00	
XVIII-1		100	12.00	12.50
XVIII-2			13.00	
XIX-1	400.0	40	1.60	1.56
XIX-2			1.53	
XX-1		70	11.82	11.42
XX-2			11.00	
XX-3		100	11.43	17.72
XXI-1			17.78	
XXI-2			17.67	
XXII-1	425.0	100	20.80	20.80
XXIII-1	500.0	40	0.20	0.18
XXIII-2			0.17	
XXIII-3			0.17	
XXIV-1		70	1.33	1.83
XXIV-2			2.33	
XXV-1		100	9.54	9.54
XXVI-1	600	40	1.00	1.00
XXVII-1		70	2.50	2.50
XXVIII-1		100	4.62	4.62

Table 3. Manometric thorium-heavy water (D_2O) vapor reaction data

Run	Temp., ° C.	Vapor pressure mm. Hg	Slope k, mg./cm. ² -log hr.
I-1	200	70	1.50
I-2			1.88
II-1	225.0	70	2.90
III-1	250.0	70	5.00
IV-1	275.0	70	3.75
IV-2			3.89
V-1	300.0	70	4.47
V-2			5.67
VI-1	350.0	70	9.01
VI-2			9.55
VII-1	400.0	70	12.90

Table 4. Gravimetric thorium-water vapor reaction data

Run	Temp., ° C.	Vapor pressure, mm. Hg	Slope k, mg./cm. ² -log hr.
I-1	200.0	40.0	1.68
I-2*			1.65
II-1		70.0	2.46
II-2*			2.28
III-1	225.0	40.0	2.80
III-2			2.50
IV-1		70.0	3.36
V-1	250.0	40.0	2.60
V-2			3.00
V-3*			2.80
VI-1		70.0	4.82
VI-2*			4.77
VII-1	275.0	40.0	3.33
VII-2			4.16
VIII-1		70.0	5.00
IX-1	300.0	40.0	3.20
IX-2			3.25
IX-3*			4.10
X-1		70	5.90
X-2*			6.75
X-3*			4.70
XI-1	350.0	40.0	7.20
XI-2*			7.18
XII-1		70.0	9.75
XIII-1	400.0	40.0	13.60
XIII-2*			13.20
XIV-1		70.0	13.50
XIV-2			12.40

* Hydrogen evolved removed through palladium thimble.

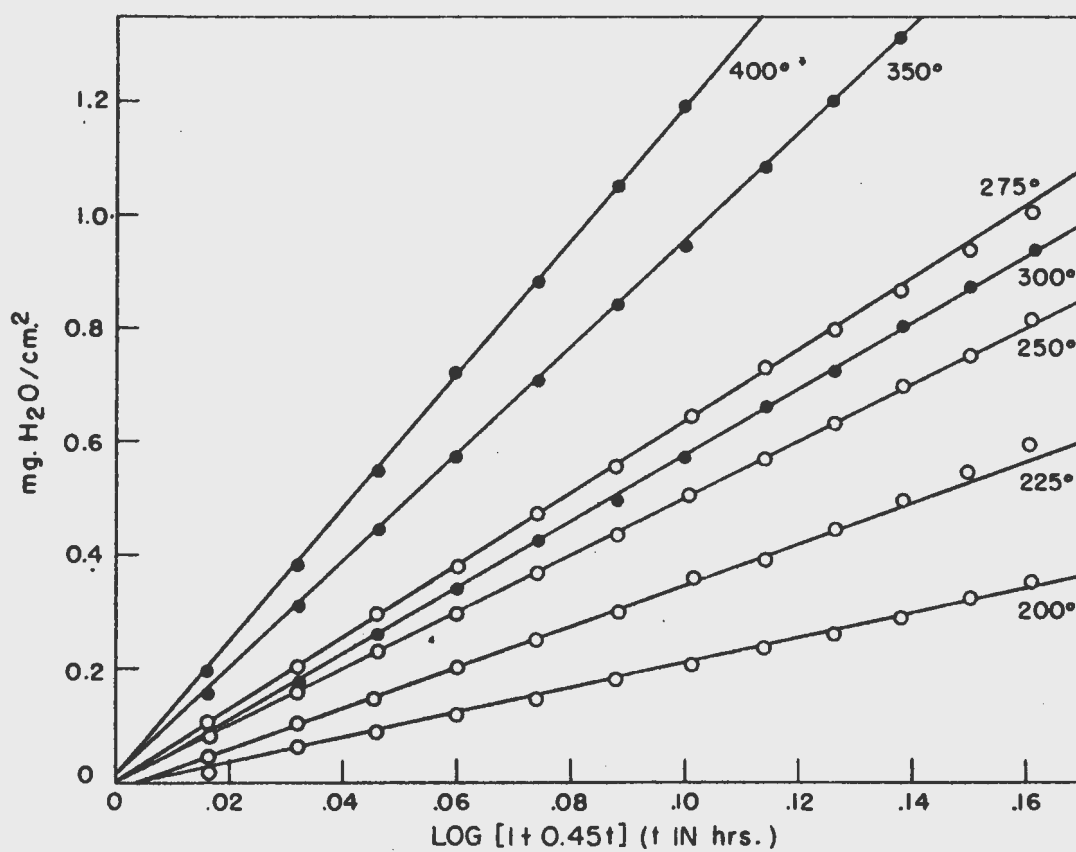


Figure 11. Logarithmic plot of thorium-water vapor data at 70 mm. Hg. water vapor pressure and varying temperatures

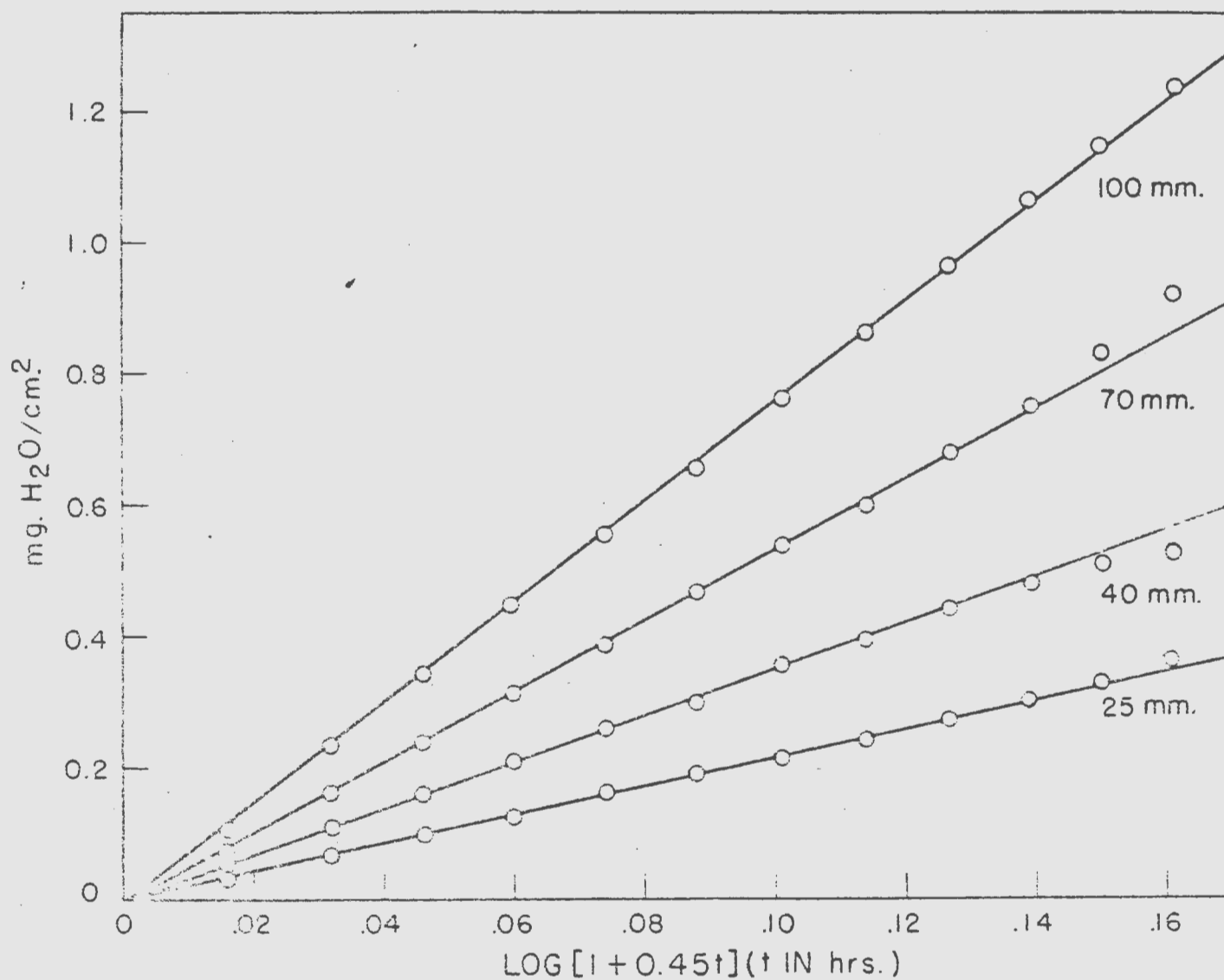


Figure 12. Logarithmic plot of thorium-water vapor data at 3000° C. and varying water vapor pressures

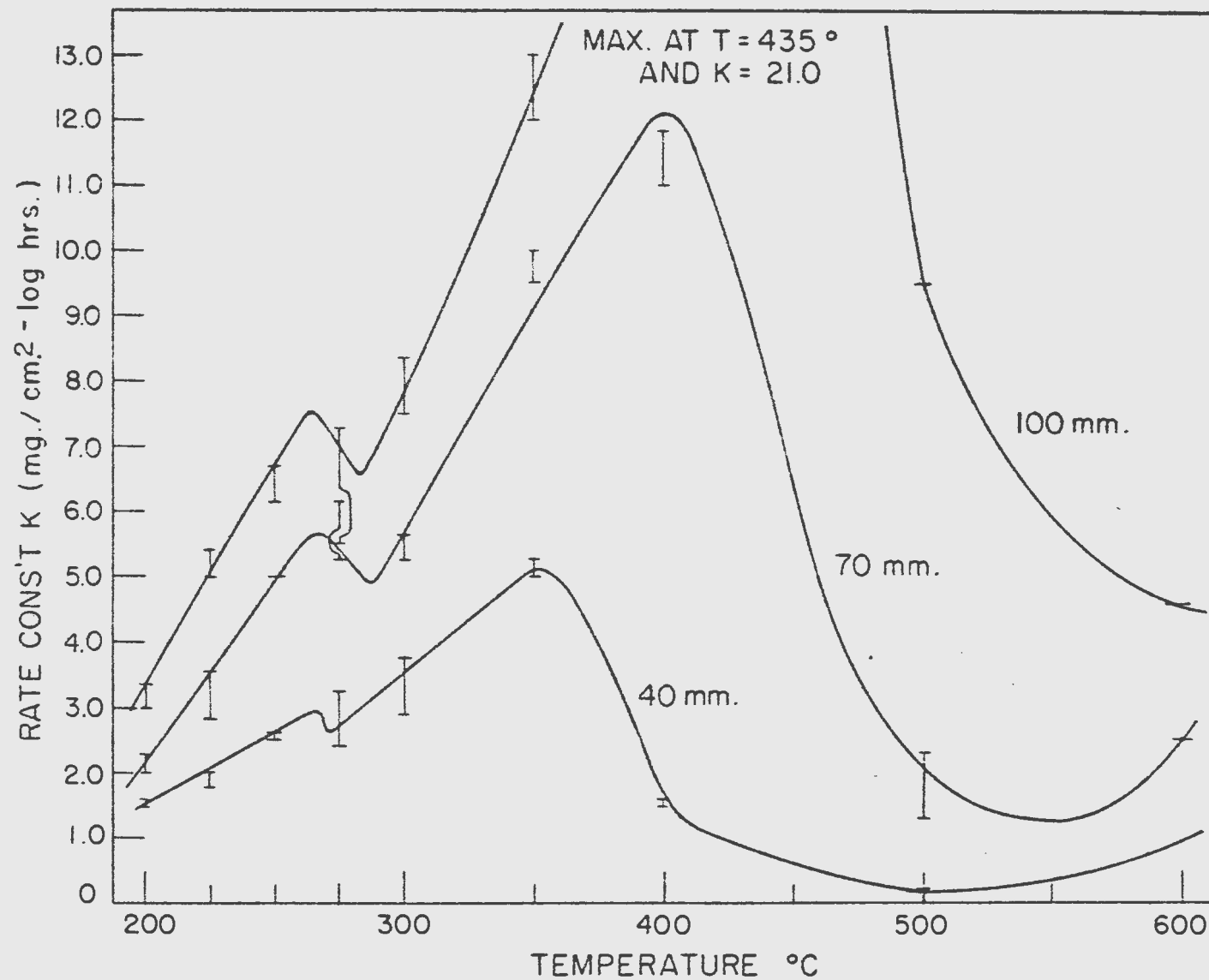


Figure 13. Effect of temperature on rate constants from thorium-water vapor data

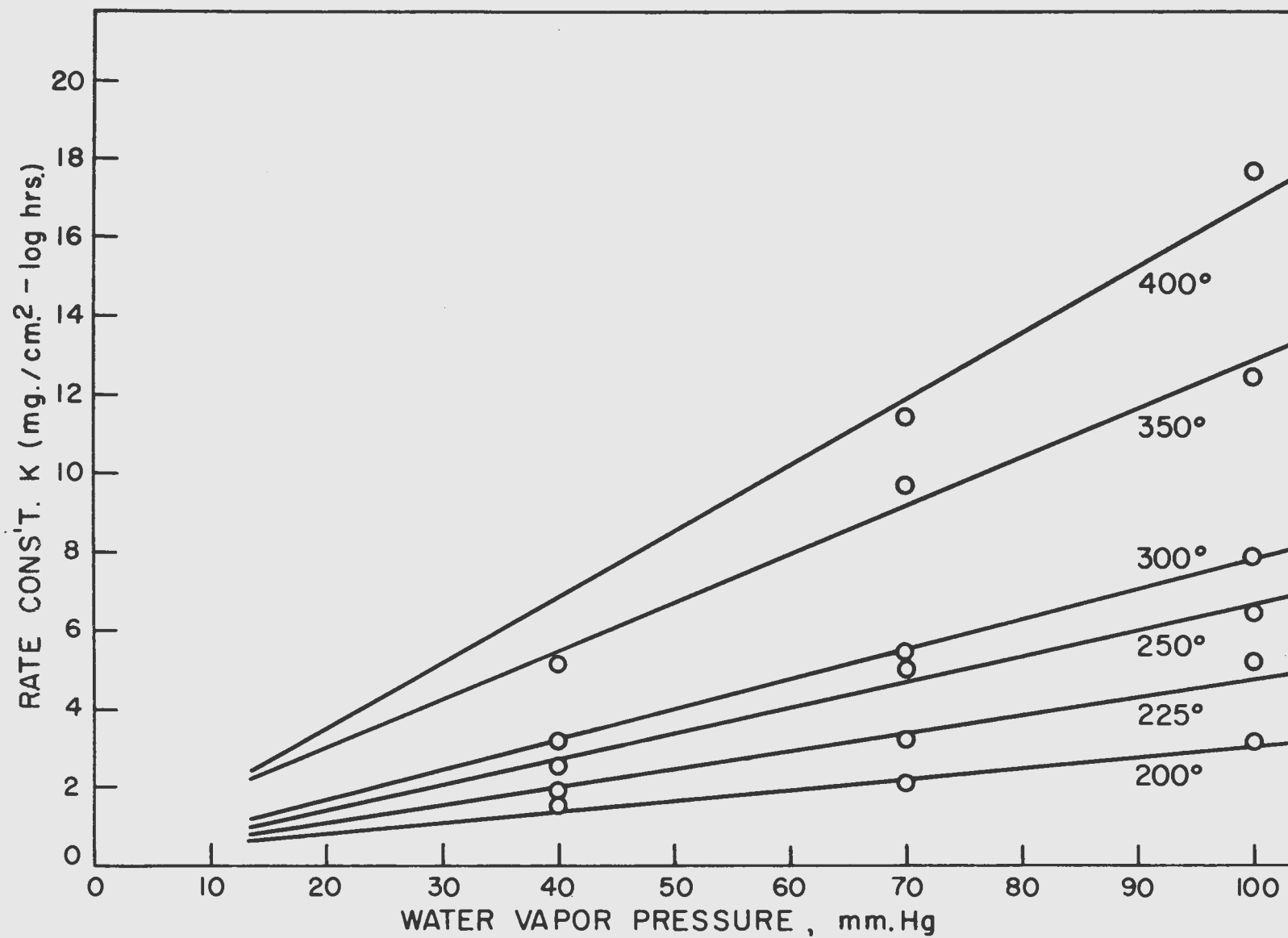


Figure 14. Effect of water-vapor pressure on rate constants from thorium-water vapor data

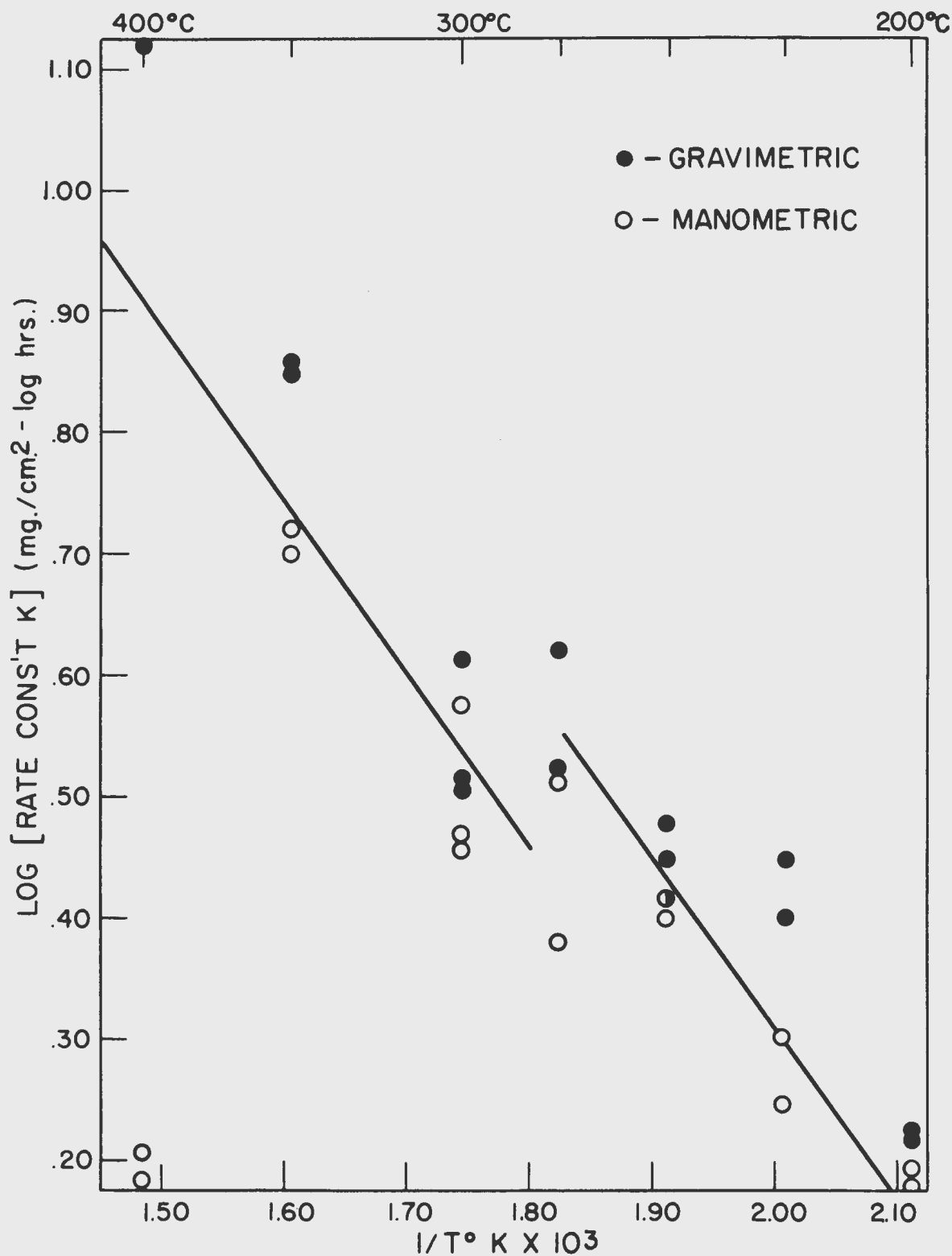


Figure 15. Log k versus 1/T at 40 mm. Hg from thorium-water vapor data

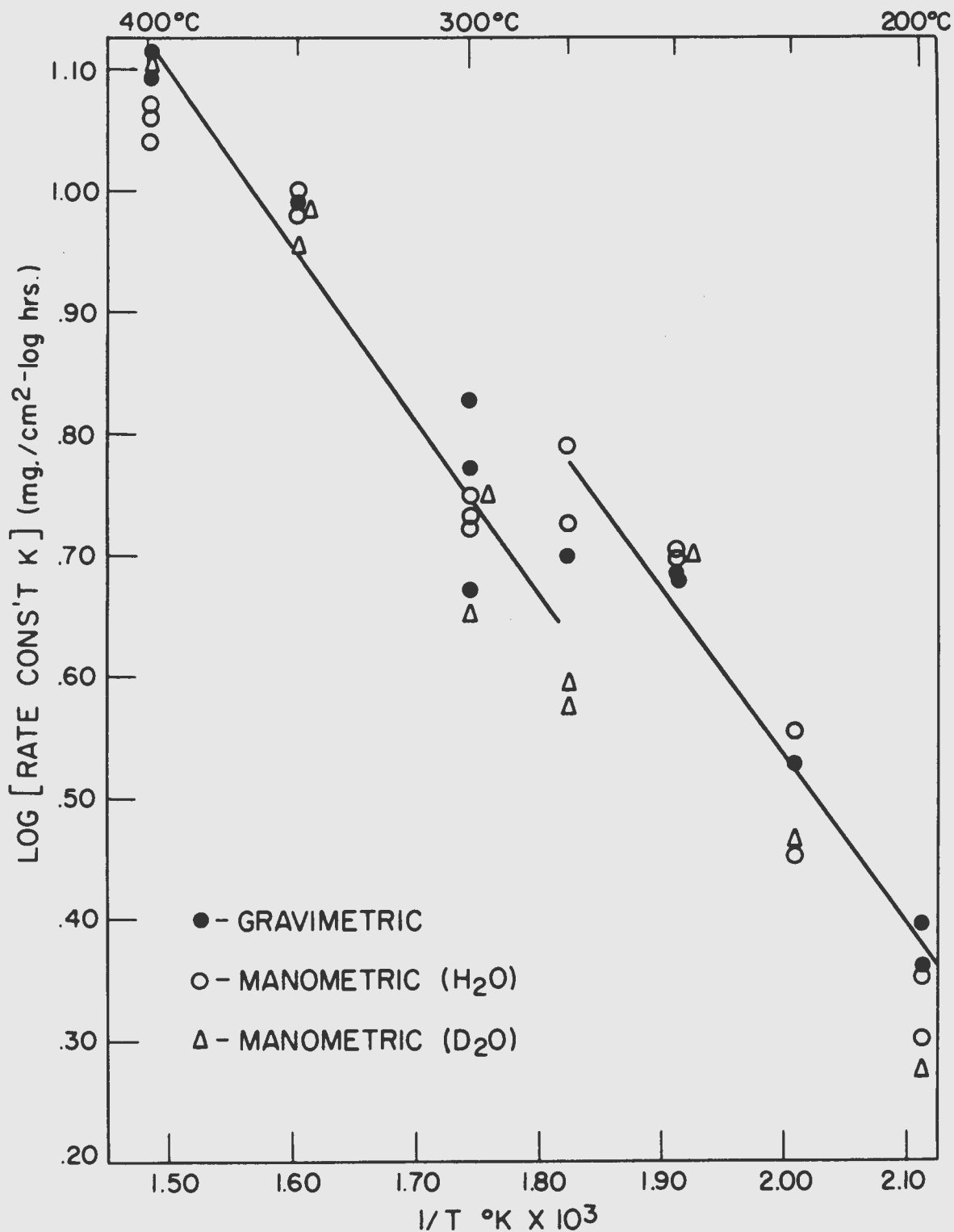


Figure 16. Log k versus $1/T$ at 70 mm. Hg from thorium-water vapor data

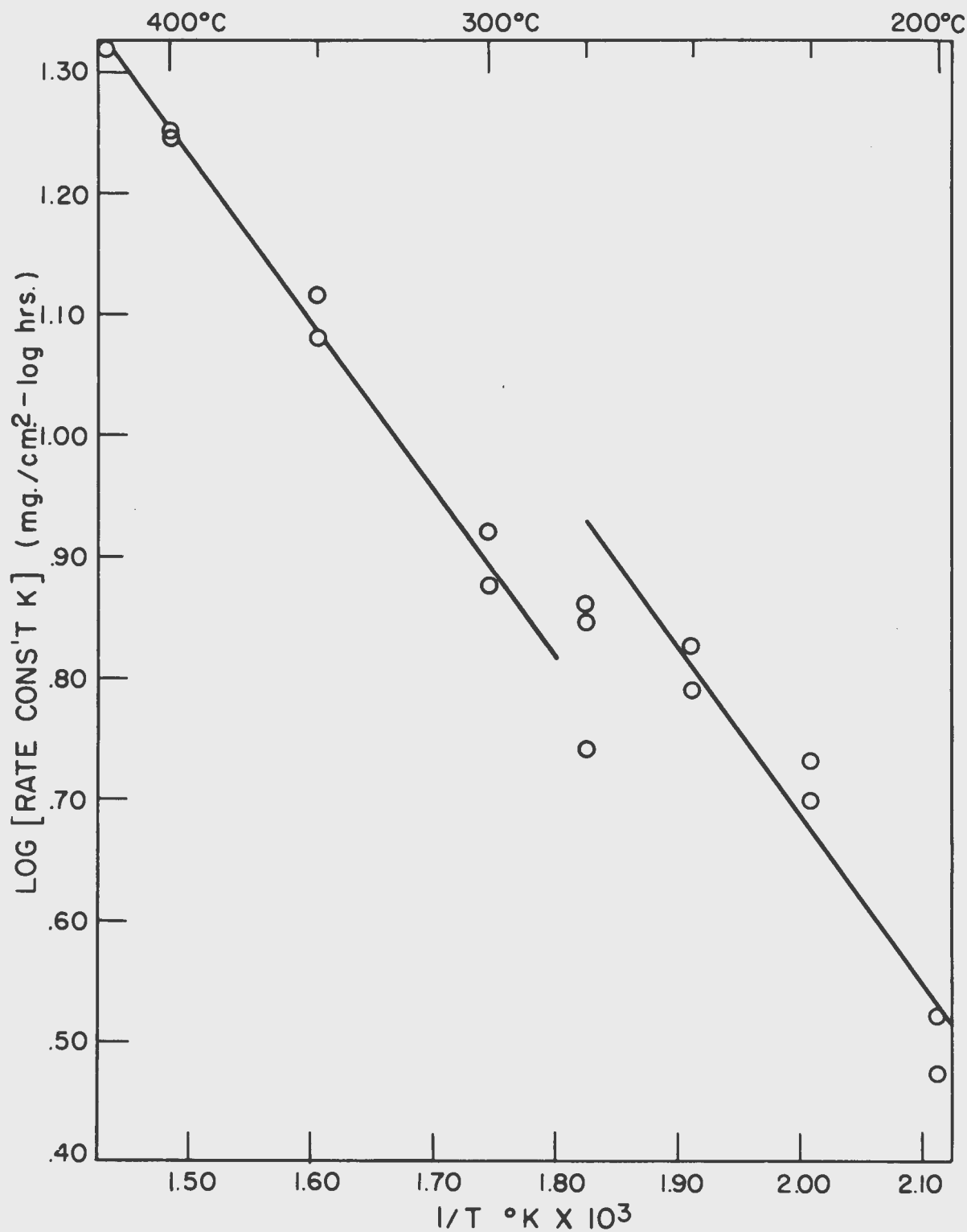


Figure 17. Log k versus 1/T at 100 mm. Hg from thorium-water vapor data

clearly divided as shown by the sudden break at 275° . Also, it is observed that on the whole, the gravimetric rates are significantly higher than the manometric by a fairly constant ratio. However, at 350° and 400° quite a variation in rates appears between the two methods. It is evident that the sudden drop in rate of the manometric reactions at this temperature may not be a real one. A following section on mechanism investigation will deal with this region more in detail.

The 70-mm. range plot shows the heavy water data in addition to the manometric and gravimetric rate constants. Again the straight lines have been drawn to fit only the manometric data, but the gravimetric rates are in close agreement with the manometric ones, or probably tend towards even a straighter line. Not too much can be said about the heavy water reaction data, since there is no significant over-all difference. In the 70-mm. plots the sudden break is more clearly observed at 275° than with the 40-mm. reactions. The 100-mm. plots in Figure 17 show the best conformity to the two straight lines. In all three pressure ranges the points at 275° are not reproducible.

In Figure 18 only the manometric data have been used for the three pressure ranges. Average values at each temperature and pressure have been used and parallel lines drawn which best fit the data. The method of least squares was used to determine slopes and thus activation energies for each set of points. Activation energies for the least square plots had values of between 5.0 and 7.2 kcal./mole showing excellent agreement. Due to the fact, however, that several of the sets contain only three points, a uniform set of parallel lines was drawn, all of which were still within the experimental error. The activation energy calculated from these parallel lines is 6.44 kcal./mole, a fairly good average. This value compares favorably with the 5 to 6 kcal. value found for the lower temperature lithium-water vapor reaction (19).

Mechanism Investigation

As mentioned in the review of the literature, several ideas have been presented concerning what species diffuses in a surface oxidation reaction on the assumption that diffusion of some species through the growing oxide layer is the rate-determining step. Several experiments were, therefore, undertaken to learn more about the mechanism of the thorium-water vapor reaction. One important fact, based on the reaction rate data, was the pressure dependence of the rate constants. In order to get a more definite relationship between pressure and rate constants, ideal rate constants were calculated from the straight lines in Figure 18. These values were then plotted against pressure, as was done in Figure 14, but with much more agreement as to first-order dependence, as is indicated in Figure 19. This indicates that the

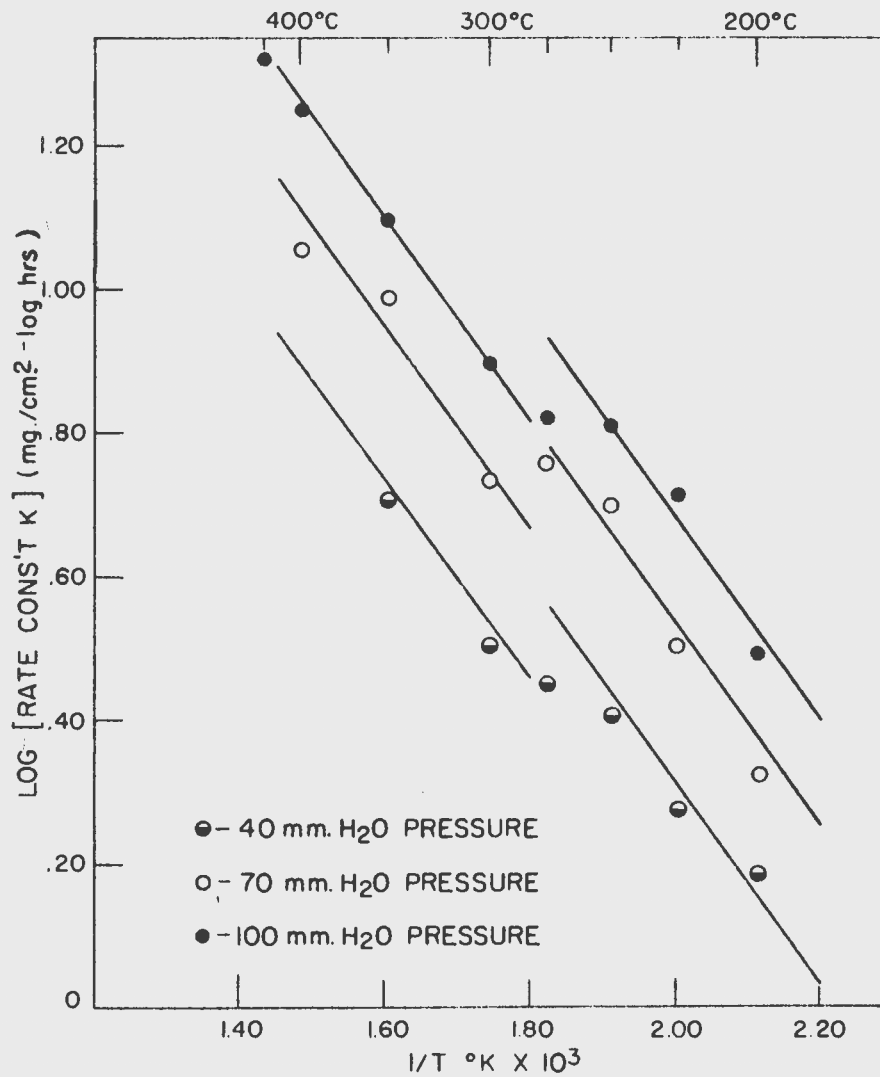


Figure 18. $\log k$ versus $1/T$ at varying pressures from thorium-water vapor data

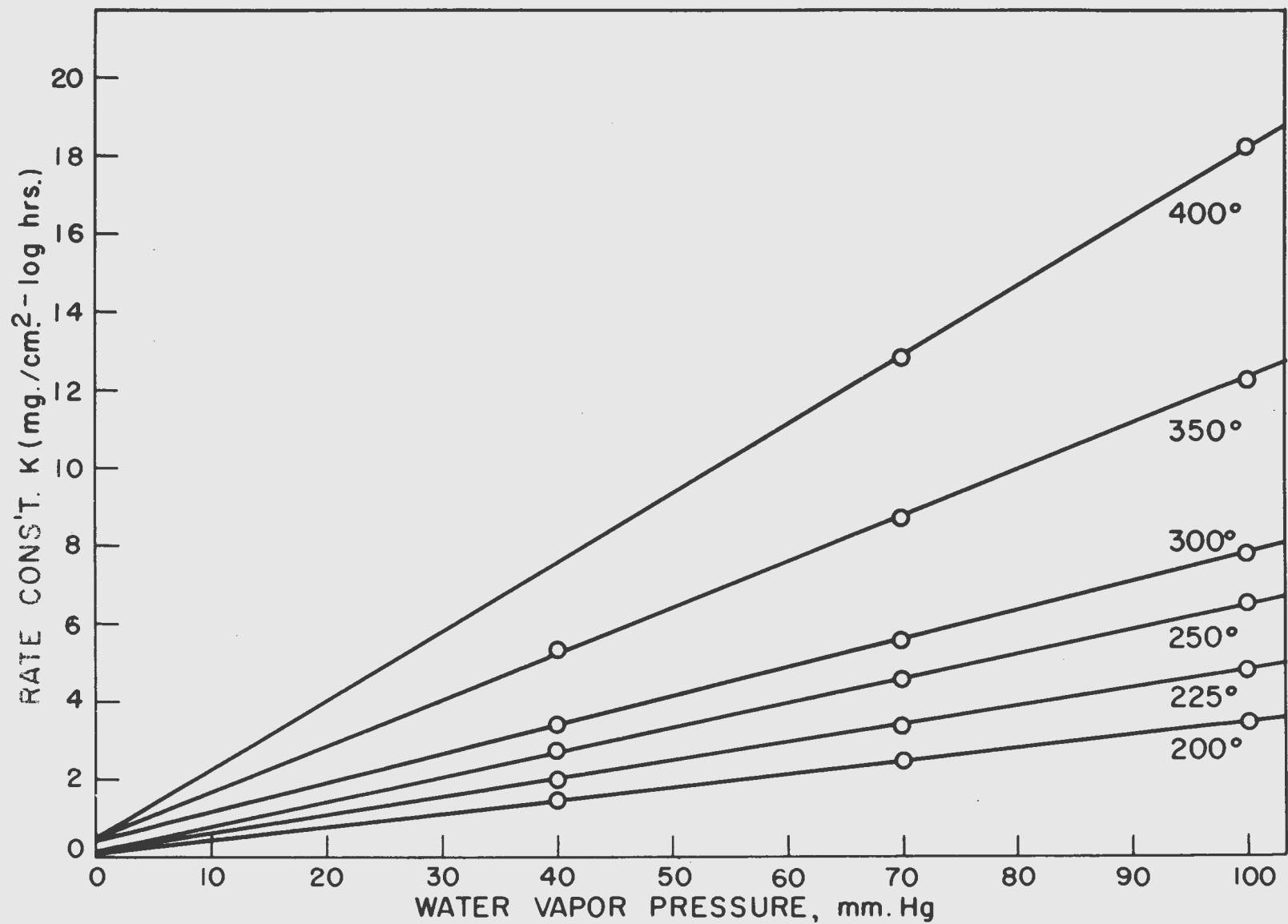


Figure 19. Water vapor pressure versus ideal rate constants showing first-order effect of pressure on thorium-water vapor reaction rates

rate determining step depends directly on the water vapor pressure, and therefore diffusion of thorium ions would be a remote possibility. As a result, if the rate of reaction is dependent on diffusion of some species through the oxide coat, diffusion of water molecules through the coat should be considered. This may be possible when a comparison of the radii of the various species involved is considered. The water molecule has a radius just a little less than the thorium covalent radius, and the Th^{+4} radius is two third the value of both. It, therefore, must be assumed that the thorium species present in this system is not entirely the ionic Th^{+4} , and that the conditions are such that the water molecules are freer to diffuse into the oxide than the thorium species to diffuse out.

Because the pressure dependence of the reactions was first order, Equation 11a appears to be valid. Since the equation states that $\text{rate} = Cpe^{-b/T} + D$, if rate is plotted against "p," the slope should be equal to $-Cp^{-b/T}$ and the intercept equal to "D." These constants were calculated from Figure 17, and the completed equations tabulated in Table 5. It is seen that the values for the constant "C" are approximately 20 and 30 for the 200° to 275° range and 300° to 400° range, respectively, with good agreement of corresponding values, and Barrer's postulate of diffusion of a single species into a solid is followed. As a comparison, Equation 9a is utilized which states that $\text{rate} = Ae^{-E/RT}$. In this case values of "A" were calculated from Figure 18 by using rate constants and activation energies already determined. Table 6 shows the equations in a form very similar to those in Table 5. The constants are observed to be about equal in value, the differences being in the intercepts of the pressure equations.

Further support of the theory of water molecules or some related species diffusing inward came from the platinum marker experiment. The position of the end of a platinum wire, which had been previously machined level with the thorium surface of a cylindrical specimen, was observed through a microscope after the cylinder had been reacted with water vapor. Microphotographs, made after sectioning and polishing the specimen, are shown in Figure 20. It is evident that the platinum extends out from the metal surface, indicating that diffusion inward of some species has taken place and reaction had taken place at the metal-coating interface. If some thorium species had diffused from the metal through the oxide layer, the oxide should have grown outward, leaving the metal surface and platinum wire in a single plane.

One fact needing explanation was the difference in rate constant values obtained by gravimetric and manometric methods in the 40-mm. pressure range, especially at higher temperatures. Since the greatest differences were at 350° to 400° C., gravimetric samples of these reactions were analyzed for dissolved or otherwise bound hydrogen by

Table 5. Pressure rate equations (rate = $-Cpe^{-b/T} + D$)

$$200.0^{\circ} \text{ C. } \text{rate} = \frac{30.14}{905} p + 0.1 = 30.14 \text{ pe}^{-\frac{3220}{473}} + 0.1$$

$$225.0^{\circ} \text{ C. } \text{rate} = \frac{30.30}{650} p + 0.1 = 30.30 \text{ pe}^{-\frac{3220}{498}} + 0.1$$

$$250.0^{\circ} \text{ C. } \text{rate} = \frac{29.94}{473} p + 0.15 = 29.94 \text{ pe}^{-\frac{3220}{523}} + 0.15$$

$$300.0^{\circ} \text{ C. } \text{rate} = \frac{20.16}{275} p + 0.40 = 20.16 \text{ pe}^{-\frac{3220}{573}} + 0.40$$

$$350.0^{\circ} \text{ C. } \text{rate} = \frac{20.30}{174} p + 0.50 = 20.30 \text{ pe}^{-\frac{3220}{623}} + 0.50$$

$$400.0^{\circ} \text{ C. } \text{rate} = \frac{20.35}{119} p + 0.50 = 20.35 \text{ pe}^{-\frac{3220}{673}} + 0.50$$

Average equation for lower temperature range:

$$\text{rate} = 30.13 \text{ pe}^{-3220/T} + 0.12$$

Average equation for upper temperature range:

$$\text{rate} = 20.27 \text{ pe}^{-3220/T} + 0.47$$

Table 6. Temperature rate equations

Lower Temperature Range

$$40 \text{ mm. - rate} = 1295 e^{-6440/RT} = 32.4 (40) e^{-6440/RT}$$

$$70 \text{ mm. - rate} = 2175 e^{-6440/RT} = 31.0 (10) e^{-6440/RT}$$

$$100 \text{ mm. - rate} = 3110 e^{-6440/RT} = 31.1 (100) e^{-6440/RT}$$

Average equation for lower temperature range:

$$\text{rate} = 31.5 (p) e^{-6440/RT}$$

Upper Temperature Range

$$40 \text{ mm. - rate} = 928 e^{-6440/RT} = 22.9 (40) e^{-6440/RT}$$

$$70 \text{ mm. - rate} = 1512 e^{-6440/RT} = 21.6 (70) e^{-6440/RT}$$

$$100 \text{ mm. - rate} = 2120 e^{-6440/RT} = 21.2 (100) e^{-6440/RT}$$

Average equation for upper temperature range:

$$\text{rate} = 21.9 (p) e^{-6440/RT}$$

a vacuum heating technique. This consisted of heating each sample to 1200°C . in a previously evacuated system and measuring the resulting gas pressure. The evolved gas was then analyzed by means of a mass spectrometer. Examined by the same method were several thorium cylinders which had previously been reacted with water vapor but which were machined down to the metal surface. Several other cylinders which had never been in contact with water vapor were similarly examined. The results were as follows:

Cylinder reacted at 400° and 40 mm.	111.00 ppm H_2
Cylinder reacted at 350° and 40 mm.	65.00 ppm H_2
Freshly machined cylinders previously reacted	33.00 ppm H_2^*
Freshly machined cylinders not previously reacted	1.13 ppm H_2^*

These results leave doubt that hydrogen was present in the metal after a thorium-water vapor reaction had taken place. The establishment of the presence of dissolved hydrogen in reacted cylinders could well be the explanation for the observed rate constant minima between 400° and 500° in Figure 13. Experiments involving removal of hydrogen by means of the palladium thimble failed to affect the minima. These results indicate that a fraction of the hydrogen released during the splitting of HOH molecules diffuses into the metal without first forming molecular hydrogen.

The metal-oxide surface is shown in Figure 20. The presence of a new and distinct intergranular phase extending into the thorium metal is observed. This phase is not ThO_2 and is presumably a thorium hydride. (A discussion of the thorium-hydrogen system has been presented in some detail by Nottorf and co-workers (31).) An intragranular phase is also present which has the same appearance in the microphotographs as the grain-boundary material, and is also presumed to be thorium hydride. Microscopic examination indicates that this material is absent in thorium which has not come in contact with water vapor in the temperature range studied. Thorium specimens, containing both these intragranular and intergranular phases after a chemical reaction with water vapor, were heated to 1200°C . in vacuo. Upon microscopic examination it was found that the phases disappeared. It is probable that the hydrogen

*Average values for several samples.

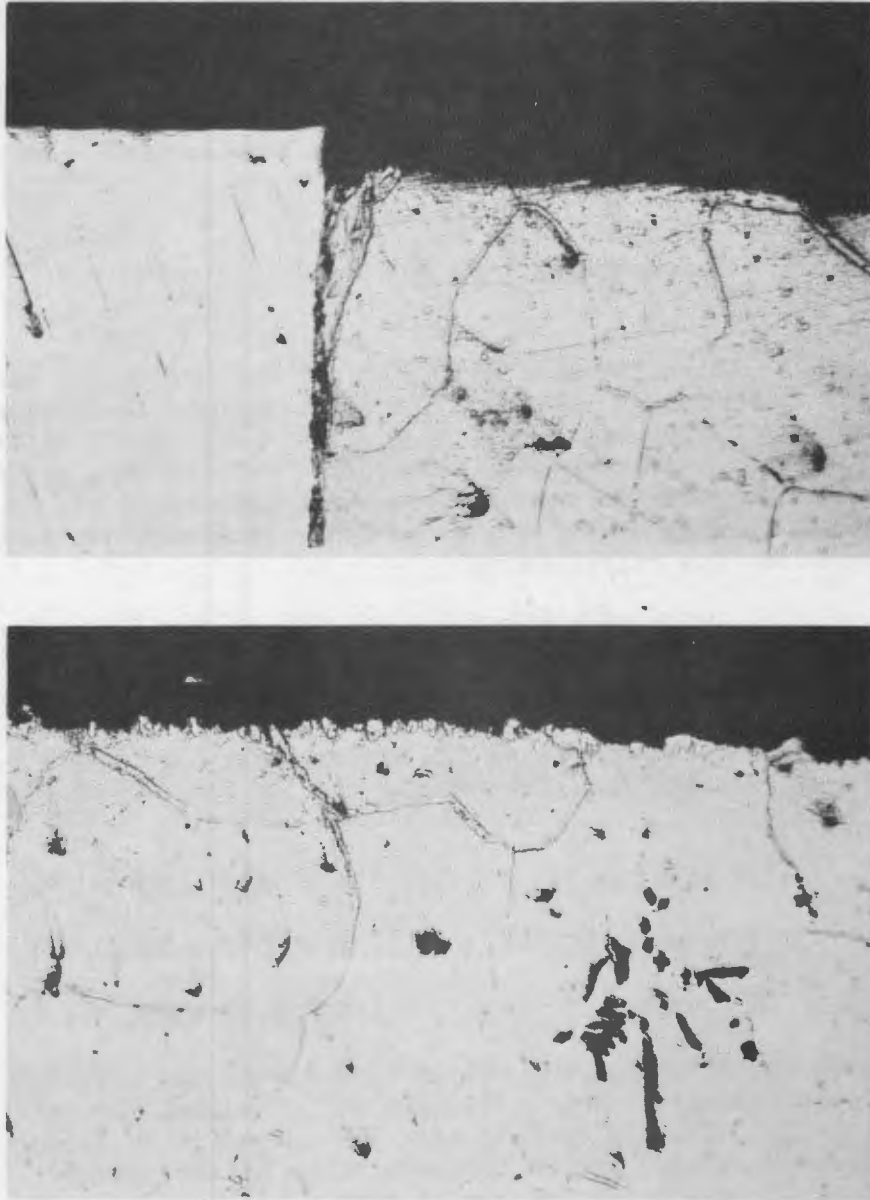


Figure 20. Microphotographs of thorium cylinder after reaction with water vapor. Top photo shows platinum wire on left extending above metal surface, indicating an inward diffusion mechanism. Lower photo shows a typical thorium surface after reaction with water vapor.

produced during the reaction between thorium and water vapor had diffused into the thorium metal and had reacted to form some type of thorium hydride.

In the derivation of the logarithmic rate law, one of the components of the constant "a" in Equation 8e was the diffusion coefficient "D." Therefore, it should be possible to calculate some sort of a value of "D" from the reaction data. The equation

$$w = \frac{g}{b} \log \left(\frac{-Dc_0 b^2 t}{g} + c' \right) \quad (8d)$$

would be used, in which the coefficient of "t" has previously been set equal to 0.45 by empirical methods. The calculation must be made at a certain time, so the assumption was made the $c = 1/2 c_0$ or, in other words, that the concentration of the diffusing species at a distance x from $x = 0$ must be equal to one half the concentration of the species at $x = 0$. If that is done and if the water vapor is assumed to be the diffusing species, the relationship

$$D = w^2 / 1.06 c_0 d_0 \quad (13)$$

is obtained, where w = weight gain per cm^2 , c_0 = concentration of diffusing species at the interface and d_0 = density of the oxide. Since the time is not known when $c = 1/2 c_0$, experimental times were taken and the equation solved for "D." The results for "D" in $\text{cm}^2/\text{sec.}$ at 300° and 70 mm. Hg are

15 minutes	$D = 2.17 \times 10^{-7}$
30 minutes	$D = 3.72 \times 10^{-7}$
45 minutes	$D = 4.60 \times 10^{-7}$

The true value of "D" may or may not be between the two extremes above, but the calculations give some indication of its value. No other water vapor-metal oxide diffusion coefficients are listed in the literature, but the values calculated are in the same range as the value 2.14×10^{-8} listed for the diffusion of nitrogen in iron (20).

LITERATURE CITED

1. Kubaschewski, O. and Hopkins, B. E., "Oxidation of Metals and Alloys," Academic Press, Inc., New York, 1953.
2. Gulbransen, E., Trans. Electrochem. Soc. 91, 573 (1947).
3. Tammann, G. and Koster, W., Z. anorg. allgem. Chem. 123, 196-224 (1922).
4. Pilling, N. B. and Bedworth, R. E., J. Inst. Metals 29, 529-582 (1923).
5. Wagner, C. and Grunewald, K., Z. physik. Chem. 40 B, 455 (1938).
6. Mott, N. F., Trans. Faraday Soc. 36, 472-483 (1940).
7. Miley, H. A., Trans. Electrochem. Soc. 81, 391-411 (1942).
8. Bangham, D. H. and Stafford, J., Nature 115, 83 (1925).
9. Vernon, W., Akeroyd, E., and Stroud, E., J. Inst. Metals 65, 301-343 (1939).
10. Alexander, W. and Pidgeon, L., Can. J. Research 28 B, 60-72 (1950).
11. Brodsky, M. and Cubicciotti, D., J. Am. Chem. Soc. 73, 3497-99 (1951).
12. Evans, U., Trans. Electrochem. Soc. 83, 335-342 (1943).
13. Dunn, J., Proc. Roy. Soc. London 111 A, 203-219 (1926).
14. Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, 1946, p. 1087-91.
15. Gulbransen, E., Trans. Electrochem. Soc. 83, 301 (1943).
16. Mott, N. and Gurney, R., "Electronic Processes in Ionic Crystals," Oxford University Press, New York, 1948.
17. Glasstone, S., Laidler, K., Eyring N., "The Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941.
18. Wilkins, F., Proc. Roy. Soc. London 128 A, 407-417 (1930).
19. Deal, B. and Svec, H., J. Am. Chem. Soc. 75, 6173 (1953).

20. Barrer, R., "Diffusion in and through Solids," University Press, Cambridge, England, 1941, p. 170.
21. Pfeil, L., J. Iron St. Inst. 119, 501 (1929); 131, 237 (1931).
22. Davies, M., Simnad, M., and Birchenall, C., J. Metals 4, 147 (1952).
23. Seaborg, G. and Katz, J., "The Actinide Elements," McGraw-Hill Book Co., New York, 1954, p. 66-102.
24. Manly, W., "Thorium," Atomic Energy Commission report 49-7-168, 1949.
25. "Report on Thorium, Thorium Oxide, and Thorium Sulfide," Atomic Energy Commission report NEPA 309, 1947.
26. Rollefson, G. and Hagemann, F., "Chemistry of Thorium," Atomic Energy Commission report CB-3717, 1947.
27. Svec, H. and Gibbs, D., Rev. Sci. Instr. 24, 202 (1953).
28. Edwards, F. and Baldwin, R., Anal. Chem. 23, 357 (1951).
29. Seybolt, A. and Burke, J., "Procedures in Experimental Metallurgy," John Wiley and Sons, New York, 1953, p. 108.
30. Kirshenbaum, I., "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Co., New York, 1951, p. 20.
31. Nottorf, R., Wilson, A., Rundle, R., Newton, A., and Powell, J., "A Physical Study of the Thorium-Hydrogen System," Atomic Energy Commission report CC-2722, 1945.